



# HANDBOOK OF NON-FERROUS METALLURGY

PREPARED BY A STAFF OF SPECIALISTS

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## CHAPTER XIX

### METALLURGY OF ALUMINUM AND ALUMINUM ALLOYS

BY ROBERT J. ANDERSON,<sup>1</sup> B. SC., MET. E., D. SC.

**Introductory.**—Aluminum is the lightest of the metals that are used in large quantities, having a specific gravity of  $2.70 \pm$ ; once obtained as pig by modern reduction processes, it can be cast, worked, alloyed, and fabricated with moderate ease; metallurgically, it is one of the most interesting metals, but not one-tenth so much scientific investigation has been given to it as to iron. The merits of aluminum and aluminum alloys have been forced upon the engineering trades against a not inconsiderable opposition, and their worth as engineering materials has been proved beyond any doubt. Aluminum has established a place for itself among the non-ferrous metals because of its intrinsic worth, and, despite its relatively high price, its consumption is increasing yearly at a rapid rate. Although aluminum is one of the most abundant metals of the earth's crust, it is at the same time one of the newest metals that has attained commercial importance.

**Historical Survey.**—Aluminum, as a metal, cannot lay claim to great antiquity, as contrasted with iron, copper, and the copper alloys, and it was a rare metal as late as 1850. Civilization is indebted to H. St. Claire Deville for the pioneer work on reduction processes for the manufacture of metallic aluminum, but other investigators had carried out work prior to the eminent French chemist. Aluminum was first isolated by Oersted in 1825, who reduced aluminum chloride with potassium amalgam. The discovery of the metal has often been credited to Wöhler, who in 1827 reduced the chloride with potassium. Up to 1845, Wöhler had been able to produce only small amounts of aluminum, but still the amounts were sufficient to determine most of its properties. The attempts of early investigators to produce aluminum are described at length in some of the older texts (cf. Richards,<sup>3</sup> Minet,<sup>4</sup> *et al.*).<sup>2</sup>

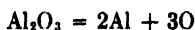
To H. St. Claire Deville the honor belongs of having isolated aluminum in fairly large amounts in 1854. Deville first made aluminum by the reduction of aluminum chloride with potassium, and later improved the process, substituting the cheaper sodium for potassium. Deville also perfected processes for the manufacture of sodium, which greatly reduced the price of both sodium and aluminum. The Deville processes, however, were all expensive and not adapted to the cheap production of aluminum in large tonnages. Aluminum was made in small amounts in France and England by the Deville-Castner sodium-reduction method until the invention of the Hall-Héroult process in 1886-1887, which drove all other processes from the field. In 1886, the Cowles process,<sup>19</sup> calling for the reduction of alumina by carbon in the presence of a metal (*e.g.*, copper) in the electric furnace, was patented and used com-

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<sup>2</sup> Throughout this chapter reference numbers apply to the appended bibliography, except in the case of obvious footnotes.

mercially. This was the first successful thermal process, but it yielded intermediate aluminum alloys and not aluminum.

In 1886, Hall in America and Hérault in Europe found independently that alumina dissolved in a liquid bath of aluminum fluoride and the fluoride of another metal yielded an electrolyte which would be decomposed by the electric current according to



The effect of the Hall-Hérault electrometallurgical method upon the price of aluminum was felt soon after 1886, and all other processes were driven from the field by 1892. In 1855, the price of aluminum was \$113 per pound, in 1890 it was \$2.38, in 1900 it was 23 cts., and in 1914 the lowest price, 19 cts., was reached. In recent years, the price has fluctuated roughly between 20 and 33 cts. per pound.

Many workers have been associated with the rise of the aluminum industry. In addition to those mentioned above there may be added the names of Davy, Bunsen, the Tissier brothers, Webster, Grätzel, Kleiner, Moissan, Ruff, Guilini, Askenasy, Bradley, Winteler, Serpek, Doremus, Krause, Grabau, Frishmuth, Netto, Welden, and Richards. The brilliant part played by Richards in the development of the aluminum industry as a consultant for the leading producers is well known.

**Producers and Output.**—The aluminum industry of the world has grown by leaps and bounds since the metal became relatively cheap commercially. In tonnage, aluminum now stands fourth among the non-ferrous metals, and it is exceeded only by copper, lead, and zinc. Richards has estimated that lead will be overtaken by 1930 and zinc by 1940. Table 1 gives the world production of aluminum over a period of years, by producing countries, and, for 1924, the distribution of output of primary aluminum by the important producing firms may be taken as shown in Table 2.<sup>1</sup>

TABLE 2.—ESTIMATED WORLD OUTPUT OF PRIMARY ALUMINUM IN 1924, DISTRIBUTED BY PRODUCING COMPANIES

Company	Main office	Reduction works in—	Output, metric tons
Aluminum Co. of America.....	Pittsburgh, Pa., U. S. A.	United States, Canada, <sup>a</sup> and Norway <sup>d</sup>	93,000
L'Aluminium Française. ....	Paris, France	France, Switzerland, and Norway	28,500
Aluminium Industrie Aktien Gesellschaft	Neuhausen, Switzerland	Switzerland, Austria, Germany	23,000
Northern Aluminium Co., Ltd. ....	Toronto, Canada	Canada	16,000
German Government-owned works <sup>c</sup>	Berlin, Germany	Germany	12,000
British Aluminium Co., Ltd. ....	London, England	England, Scotland, Norway	10,000
L'Aluminio Italiano <sup>b</sup> ....	Milan, Italy	Italy	2,000
Aluminium Corporation, Ltd. ....	Dolgarrog, Wales	Wales	1,000
Total...			185,500

<sup>a</sup> The present producing plants in Germany are the Erftwerk, the Lautawerk, and the Innwerk.

<sup>b</sup> Including Società per la Fabbricazione dell' Aluminium.

<sup>c</sup> Plant of subsidiary, the Northern Aluminium Co., Ltd., in Canada; output given under this company.

<sup>d</sup> Plant of subsidiary, the former Norsk Aluminium Co., in Norway; output in 1924, about 8,000 metric tons.

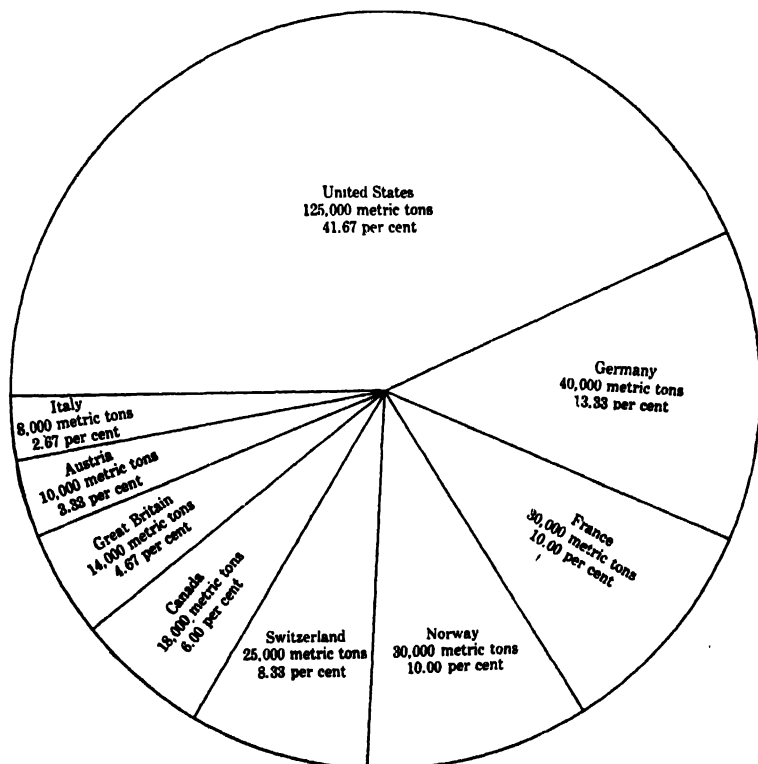


FIG. 1.—Aluminum reduction-cell capacity of the world.

Total reduction-cell capacity of the world is now about 300,000 metric tons, and the relative capacity of the different producing countries is about as shown in the accompanying diagrammatic wheel of Fig. 1.

A recent development of great importance is the new hydro-electric powerplant and aluminum works of the Aluminum Co. of America, now (1925) under construction at Chute a Caron on the Saguenay river in Canada. This will markedly increase the present capacity of the company.

The political control of both the bauxite mines and the aluminum-reduction plants of the world is largely in the hands of the United States, Great Britain, France, Germany, and Switzerland, and the principal aluminum-producing countries of the world, as of 1924, were the United States, Norway, Switzerland, France, Canada, Germany, Great Britain, Austria and Italy, in the order named. For many years, the United States has turned out about 50 per cent of the world's production. A number of countries, including Australia, Belgium, India, Japan, and Sweden, are consumers of aluminum but do not produce primary metal. The aluminum-production situation has been discussed in detail by Richards,<sup>26</sup> the writer,<sup>18, 73</sup> and Fox.<sup>74</sup>

**Markets and Trade Statistics.**—In general, the consumption of foreign producing countries is much less than the supply, but in the United States, under normal conditions, the domestic output is by no means equal to the demand. The United States, therefore, is compelled to import substantial amounts of primary aluminum pig, and imports in 1924 were about 29,000,000 lb., as compared with production of about 187,000,000 lb. Imports came largely from Norway, Canada, Switzerland, and Great Britain. Aluminum exports from the United States have generally been small. Table 3 gives a summary of the imports of aluminum into the United States by countries of origin. There is a general absence of any trading market in the United States for primary aluminum, since prices are controlled by the Aluminum Co. of America, and importers sometimes offer foreign metal at  $\frac{1}{2}$  to 1 ct. per pound under the domestic price.

Detailed statistical data covering production, imports, and exports, etc. are given yearly by the writer<sup>73</sup> in the *Mineral Industry*, by Hill,<sup>46</sup> by the Imperial Mineral Resources Bureau,<sup>88</sup> and by the Metallgesellschaft.

In the United States, import duties on aluminum and manufactures thereof have been levied for many years. Under the old Underwood-Simmons Act, the import duty on aluminum, aluminum scrap, and aluminum alloys was 2 cts. per pound, and that on sheets, coils, plates, bars, rods, and related semifinished manufactures was  $3\frac{1}{2}$  cts. Under the later Payne-Aldrich Act, these duties were 7 and 11 cts., respectively, and under the present Fordney-McCumber law, the duties are 5 and 9 cts., respectively. In general, the price of aluminum in the United States has been increased in the past in about the same proportion as the duty on foreign metal has been increased.

**Aluminum Ores, and Bauxite Mining.**—Aluminum is the most abundant of the commercial metals and is third in abundance of the elements in the earth's crust, following oxygen and silicon. Aluminum is nearly twice as abundant as iron, and constitutes about 7.85 per cent of the earth's crust (Clarke). Aluminum is an essential constituent of all important rocks, except the sandstones and limestones, but even in these its compounds are common impurities. Aluminum



FIG. 2.—Microstructure of bauxite pisolite with oölitic matrix;  $\times 11$ . (Shearer.)

never occurs native, and, except for its fluorides, it invariably occurs as oxidized compounds. Thus, it is found mainly in the silicates, such as the clays, micas, and feldspars; as the oxide, corundum; as the hydroxide, bauxite; as the fluoride, in cryolite; and also in various phosphates and sulphates. Although aluminum minerals occur widely, few of these can be employed as ores in the manufacture of aluminum, and in the present commercial production of aluminum only two aluminum minerals are utilized, *viz.*, bauxite and cryolite. Bauxite is the base ore for aluminum reduction and bears the same relation to aluminum that hematite does to iron. Cryolite is the basis of the reduction-cell bath.

**Bauxite and Related Minerals.**—Theoretical bauxite has been given the formula  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , but the usual ore has chemical composition midway between diaspore ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) and gibbsite ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ); sometimes it is near the one and sometimes near the other. Bauxite is an earthy mineral and never crystal-



lized; it occurs in a variety of forms, but usually has a pisolitic or oolitic structure, with rounded concretionary grains embedded in a clay-like mass. The color ranges from light cream through various shades of brown to a deep brownish red, depending on the iron content. Bauxite takes its name from the village of Baux, near Arles in France, where it was first found by Berthier. The following physical properties of bauxite may be noted as an aid to identifying the mineral: hardness, 1 to 3 (Moh); specific gravity, 2.55; melting point—on heating it changes to  $\text{Al}_2\text{O}_3$ , which, when pure, melts at 1880 to 2050°C.; index of refraction, 1.57; color, white, cream, yellow, brown, gray, or red; streak, variable; luster, dull to earthy; cleavage, irregular fracture; transparency, opaque; tenacity, crumbly. Diaspore and gibbsite are associated with bauxite and found under the same conditions. Laterite is an aluminous ore, which is essentially a mixture of iron hydrate, aluminum hydrate, and silica in varying proportions. The Indian aluminum ores are laterites. Figure 2 shows the microstructure of a hard, high-grade, pisolitic bauxite from Georgia.

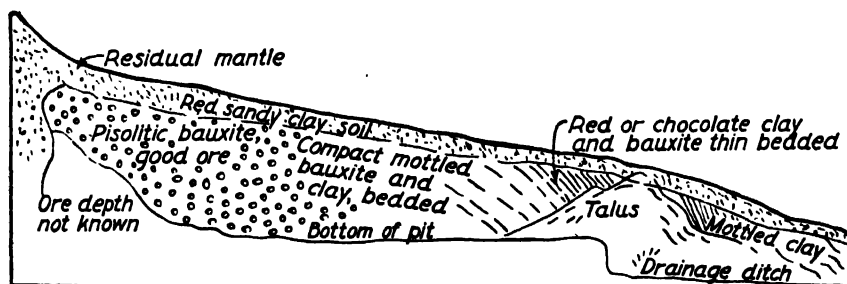


FIG. 3.—Typical bauxite deposit. (Hayes.)

Various theories have been advanced by geologists to account for the deposition of bauxite in the earth's crust. Bauxite occurs under a variety of conditions which suggest dissimilarity of origin, and no one theory appears to account for all cases. Some bauxites are regarded as decomposition products of granites, syenites, gneisses, and basalts, while others have apparently been derived by solution of the alumina from sedimentary rocks, such as shales, followed by deposition in limestones and dolomites. It is well established that bauxite may be formed by more than one geological process; it occurs *in situ*, as does laterite, as a residue from the decomposition of rocks; it is found also, evidently, as a precipitate; and at times it occurs like any other disintegration product in beds representing transported material. The superficial concentration of bauxite is analogous to that of iron ores, and in some deposits both are found together. Just as iron ores are concentrated from dunite, peridotite, or greenalite and sideritic rocks, so bauxite is concentrated from nepheline syenite, clayey limestone, and other rocks rich in aluminum, and particularly from those that furnish abundant alkaline solutions to aid in the removal of silica. Figure 3 shows a section of a typical bauxite deposit. The theory of deposition has been discussed by Hayes,<sup>22</sup> among others.

**Commercial Bauxites.**—Bauxite occurs at a number of places in the world, but high-grade deposits are not numerous. Commercial bauxite ore is an hydrated oxide of aluminum, or a mixture composed of at least two and probably three hydrates, mixed with various impurities, chiefly iron oxide, silica, clay, and titania. Other impurities present are calcium oxide, magnesia, potassium oxide,

and sodium oxide, in subordinate amount. The water content, both mechanical and combined, is variable over a wide range. Table 4 gives the chemical composition of some bauxites from various sources, which will serve to indicate the range of a variety of deposits. The color of bauxites varies considerably depending upon the iron-oxide content, being whitish when silica is predominant and red when iron oxide is present in important amount. In a general way, the range of composition of bauxites is as follows: alumina, 45 to 70; silica, 2 to 30; ferric oxide, 3 to 25; and loss on ignition, 12 to 40 per cent. About 3 per cent of titania is associated with these oxides, and this is characteristic. Bauxites may be roughly classified, on the basis of their impurities, as follows: (1) high in iron and low in silica (red varieties); (2) low in iron and high in silica (white and gray), and (3) iron and silica contents about the same, either high or low. Bauxite is graded according to chemical composition and sold to the consuming industries on the basis of chemical analysis. The grading and the marketing of bauxite have been discussed by Hill<sup>46, 49</sup> and Ladoo.<sup>78</sup>

TABLE 4.—ANALYSES OF SOME BAUXITES FROM VARIOUS SOURCES<sup>1</sup>

Source	Chemical composition, constituents per cent						
	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Loss on ignition	Other constituents	Total
United States:							
Arkansas*	10.0	4.0	52.0	4.0	30.0	.....	100.00
Arkansas*	4.0	4.0	53.0	10.0	29.0	.....	100.00
Alabama*	2.10	3.12	61.0	2.20	31.58	.....	100.00
Alabama	21.08	2.52	48.92	2.19	23.86	P <sub>2</sub> O <sub>5</sub> , trace	98.57
Georgia.	6.62	1.05	64.91	0.28	33.53	.....	100.39
Georgia	9.08	3.44	57.28	0.96	29.12	.....	99.88
Austria:							
Sonnthal	6.32	0.91	64.05	15.93	13.28	.....	100.49
Feistritz	13.60	..	57.25	0.97	24.38	CaO, 1.80; P <sub>2</sub> O <sub>5</sub> , 1.40	99.40
Croatia:							
Rudopolje	6.30	..	66.02	14.82	12.70	.....	99.84
Grgienbrig.	10.29	..	50.61	26.89	11.29	.....	99.08
Dalmatia:							
Mosée.	0.87	..	59.27	24.36	15.93	.....	100.43
Ilvar....	30.47	..	29.05	16.24	17.14	CaO, 6.79; MgO, trace	99.69
France:							
Var....	0.30	3.40	69.30	12.90	14.10	.....	100.00
Bouches-du-Rhône.	4.80	3.20	55.40	24.80	11.60	.....	100.00
Germany:							
Garbenteich	1.10	3.20	50.92	15.70	28.80	CaO, 0.80; MgO, 0.16	100.58
Firnewald...	4.92	2.80	53.10	10.62	27.80	CaO, 2.62; MgO, trace	99.86
Hungary:							
Bihárhegyesg.	6.69	3.10	58.70	19.23	11.80	CaO, 0.80	100.32
Királyerdő	1.62	1.15	60.83	25.82	11.31	.....	100.73
Ireland.							
Antrim	6.01	....	61.80	1.96	27.82	.....	97.98
Antrim.	15.05	....	43.44	2.11	35.70	.....	96.30

\* Approximate composition.

<sup>1</sup> From different published analyses.

Bauxites are used for abrasives, for chemical and refractory manufacture, and for the preparation of high-alumina cements, as well as for aluminum reduction, and the grade of ore required is variable, depending upon the use. For different uses, the grades of bauxite designed in American practice are as follows:

For aluminum manufacture: alumina ( $\text{Al}_2\text{O}_3$ ), more than 52 per cent; silica ( $\text{SiO}_2$ ), less than 4.5; and ferric oxide ( $\text{Fe}_2\text{O}_3$ ), less than 6.5 per cent.<sup>\*</sup> (At the present time, bauxite carrying less than 50 per cent  $\text{Al}_2\text{O}_3$  and up to 7 per cent  $\text{SiO}_2$  is being used.) High-grade bauxites for aluminum manufacture often contain 58 to 65 per cent  $\text{Al}_2\text{O}_3$ , as little as 1 per cent  $\text{Fe}_2\text{O}_3$ , and 3 to 5 per cent  $\text{SiO}_2$ .

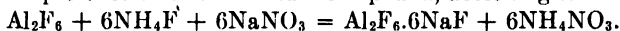
For chemical purposes (alum and aluminum sulphate preparation): alumina ( $\text{Al}_2\text{O}_3$ ), more than 52 per cent; low ferric oxide and titania are preferable, *e.g.*, less than 3 per cent of each, but for some uses less pure ores are employed; requirements on silica are not set, but bauxites containing up to 19 per cent  $\text{SiO}_2$  are used. It is definitely required that the alumina shall go readily into solution in dilute sulphuric acid.

For abrasives: various grades of bauxite are employed, but those low in iron and titanium are preferred. Generally, the requirements are: less than 5 per cent  $\text{SiO}_2$ , preferably 3 per cent;  $2\frac{1}{2}$  to 4  $\text{TiO}_2$ ; and 3 to 5 per cent  $\text{Fe}_2\text{O}_3$ .

For refractories: the principal requirement is low iron and titanium contents, but the silica may be fairly high. So-called high-alumina clays, containing 48 to 52 per cent  $\text{Al}_2\text{O}_3$ , and high-grade diaspor, containing up to 80 per cent  $\text{Al}_2\text{O}_3$ , are now used in the refractory industry.

Table 5 shows the world production of bauxite.

**Cryolite.**—Cryolite is an aluminum mineral of the composition  $\text{Na}_3\text{AlF}_6$  (or  $3\text{NaF} \cdot \text{AlF}_3$ ), required in the production of aluminum, being the chief constituent of the electrolytic bath and used to dissolve the alumina. The actual composition of pure cryolite is 32.8 per cent sodium, 12.8 per cent aluminum, and 54.4 per cent fluorine. The only commercial source of cryolite is the deposit at Ivigtut, Aarsua, South Greenland, owned by the Kryolith Mine & Handels-selskabet, A/S, of Copenhagen, Denmark. The high price of cryolite has led to the production of artificial cryolite, and this is now used generally in aluminum manufacture. Methods of preparation for artificial cryolite are described by Pattison,<sup>8</sup> Mortimer,<sup>12</sup> and others. In a patented process by Howard,<sup>1</sup> the artificial product is prepared by the interaction of aluminum fluoride and sodium fluoride in the presence of an ammonium compound, according to



In the Hulin process, pure hydrated alumina is treated with hydrofluoric acid, and the resulting product is saturated with sodium dioxide, giving artificial cryolite.

**Other Aluminum Minerals.**—A few other aluminum minerals may be mentioned. Alunite ( $\text{K}_2(\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 6\text{H}_2\text{O})$ ) is an hydrous sulphate of aluminum and potassium, found in many places, and worked at Tolfa, Italy, and in Utah and Colorado. Alunite has been studied considerably as a source of both alumina and potash. Corundum is the sesquioxide of aluminum ( $\text{Al}_2\text{O}_3$ ). It does not occur in sufficiently large deposits to make it an ore, but it was formerly used in the Cowles process for manufacturing aluminum alloys. The feldspars are an important group of rock-forming minerals containing aluminum, but none of these is an ore. The feldspars vary widely in composition and include such minerals as orthoclase ( $\text{KAlSi}_3\text{O}_8$ ) and anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ). Labradorite, a feldspar, found in large quantities in Norway, has been used experimentally as a source of alumina for aluminum manufacture. Leucite, potassium-aluminum metasilicate ( $\text{KAl}(\text{SiO}_3)_2$ ), has been employed experimentally as a source of both alumina

<sup>1</sup> U. S. Patents, 1511560 and 1511561, Oct. 14, 1924.

and potash. The well-known china clay, kaolinite, is a basic orthosilicate of aluminum, corresponding to  $H_4Al_2Si_2O_9$ , and is one of the most important minerals of aluminum. The mineral kaolin is known variously as white china clay, pure white clay, and fuller's earth. The great purity of high-grade kaolin and the large available deposits stamp it as the logical ore for the manufacture of aluminum, but it cannot be now employed because of the cost of separating the alumina from the silica. Common clays are simply very impure kaolins. Sillimanite, cyanite, and andalusite are three aluminum minerals of great importance to the ceramic industry because of their conversion on firing to a compound known as mullite or artificial sillimanite, which latter possesses very useful properties. The formula for sillimanite, cyanite, and andalusite, is  $Al_2O_3 \cdot SiO_2$ . Myers<sup>113</sup> discusses the occurrences and uses of sillimanite, cyanite, and andalusite. There are many other aluminum-bearing minerals, but space prevents mention of them here.

<sup>1</sup> Based on statistics prepared by the writer for the *Mineral Industry*.

<sup>a</sup> Unofficial figures

<sup>b</sup> Figures not yet available.

<sup>c</sup> See Austria.

<sup>d</sup> Estimated

<sup>e</sup> No record of any production prior to 1920.

<sup>f</sup> Reported under Jugo-Slavia

<sup>g</sup> Istria included under Italy

<sup>h</sup> Mines closed early in 1921 and not opened until December, 1922.

**Bauxite Mining and Preparation.**—Bauxite is mined ordinarily by open-pit methods, since the producing bodies are near the surface. Ladoo<sup>78</sup> has discussed the mining operations of the American Bauxite Co., in Arkansas, which are typical of large-scale production. The ore bed at Bauxite, Saline County, runs about 11 ft. thick, and the overburden is 25 to 140 ft. thick. In mining, the overburden is first stripped off by steam shovel, and the stripped surface is then

cleaned and swept. The ore is loosely consolidated, but it is usually too hard to be mined without blasting. Low-strength dynamite is used for blasting. The loosened ore is loaded by steam shovel on cars. Figure 4 shows the mining of bauxite with steam shovels at a mine of the American Bauxite Co., at Bauxite, Ark. In 1924, the American Bauxite Co. started underground mining at its Bauxite, Ark., properties in order to overcome heavy stripping costs. In the Georgia-Alabama-Tennessee district, the ore occurs in lenticular and irregular deposits which do not lend themselves to steam-shovel operation, and all mining is done by hand.

It should be pointed out that the concentration or beneficiation of loosely consolidated bauxite mixed with clay has been tried at a few mines in the United States, using log washers, but this practice is now rare here. In Germany, ores from many small concessions in Hesse are washed at a central washing plant. Recently, considerable interest has been displayed in the possibility of beneficiation of low-grade bauxites and bauxitic clays because of the dwindling of high-grade bauxite. Everhart has shown that clay can be separated from bauxite by washing in the presence of small amounts of added peptizers, *e.g.*, sodium hydroxide and the more strongly adsorbed sodium salts.



FIG. 4.—Mining bauxite with steam shovels, Bauxite, Ark.

Bauxite, when mined, may be given preliminary treatment on the ground, depending upon the nature of the ore. The bauxites found in the United States ordinarily contain 15 to 33 per cent of combined water, together with a varying amount of mechanically held moisture, and, since the ores must ordinarily be shipped long distances, it is usual to dry the ore at the mines so as to save freight and to facilitate fine grinding for later use. For the preparation of alumina to be used in the manufacture of aluminum, bauxite is ordinarily crushed and dried at the mine, but not ground finely. In crushing, the crude ore is run through gyratory or other types of rock breakers and crushed to small nut size. Gyratory breakers are generally used for hard ores and disintegrators for soft ores. It is desirable to calcine most bauxites in order to remove organic matter which would interfere with the precipitation of aluminum hydroxide in the preparation of alumina, to oxidize ferrous oxide to ferric oxide, and to remove water which may be present in sufficient amount to form a

pasty mass and clog the screens in fine grinding. For calcination, the ore may be heated at about 600°C. in cylindrical rotary kilns of the type shown in Fig. 5. By such treatment, the moisture content is reduced to  $\frac{1}{2}$  to 1 per cent. Kilns for calcination are 3 to 7 ft. in diameter and 30 to 50 ft. long.

**Markets and Trade Statistics.**—The market for bauxite is always rather variable in the absence of trading, since consumers either largely control their own supplies or else are covered on long-time contracts with mines. In the open market, domestic bauxite is sold on the long-ton basis at a price, f.o.b. cars, point of shipment. Imported French bauxite is quoted per metric ton, c.i.f. Atlantic ports. Typical selling prices in 1924 for domestic ore were: \$5.50 to \$8.75 per ton for the dried, \$12 to \$14 for the crushed, and \$20 for the calcined. French ore sold at \$5 to \$8. The present duty on bauxite imported into the United States is \$1 per long ton, and that on alumina is 1 c. per pound. The principal markets for bauxite in the United States are east of the Mississippi River. Marseilles, France, and Fiume, Italy, are large shipping centers in Europe.

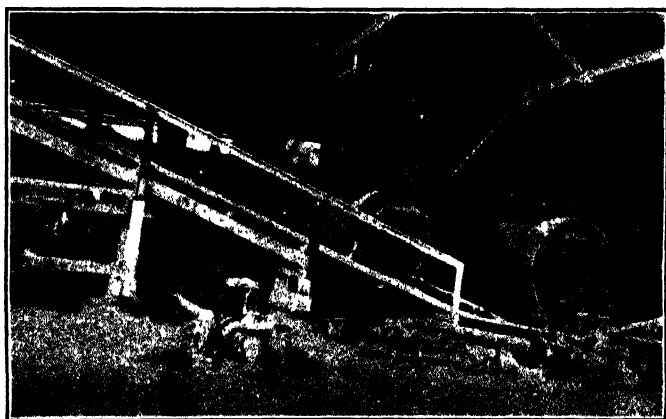


FIG. 5.—Rotary calcining kilns.

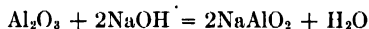
**Production of Aluminum.**—For the past thirty-five years, the production of metallic aluminum on a commercial scale has been carried out in two essential steps: (1) the preparation of alumina of high purity from bauxite, and (2) the electrolysis of the alumina in a liquid bath of cryolite plus other added salts. The reduction of alumina ( $\text{Al}_2\text{O}_3$ ) to aluminum cannot be done by carbon smelting, as with iron, copper, lead, and other commercial metals. Or, more precisely, alumina can actually be reduced by carbon, but, at the temperature and conditions of such reduction, the aluminum so reduced either volatilizes, oxidizes, or interacts with carbon monoxide or dioxide, forming aluminum carbide or aluminum oxide. Modern processes for aluminum reduction depend primarily upon the preparation of substantially pure alumina, and this is the first step in the treatment of bauxite after calcination and grinding.

As pointed out previously, crude bauxite ore contains varying amounts of ferric oxide, silica, titania, and other impurities; these oxides must not be present in the alumina which is added to the electrolytic bath, since otherwise the reduced metals, iron, silicon, etc. will appear in the resultant aluminum. It should be emphasized

that one of the chief difficulties in the metallurgy of aluminum lies in the fact that the metal, after being produced, cannot be refined, as can copper and other of the commercial metals, and the purity of the metal secured by electrolytic dissociation depends primarily upon the purity of the alumina and the electrolytic bath. Many patents have been issued which apparently cover every conceivable method for obtaining aluminum from aluminum-bearing minerals, but the only commercial process is that one calling for the electrolytic dissociation of alumina dissolved in a liquid bath of cryolite plus other added salts. Electrolytic methods for the dissociation of aluminum compounds are not applicable in aqueous solution, and fused electrolytes must be employed. For the electrolytic process, a primary requisite for commercial practice is a source of cheap electric current, since an enormous amount of current is required, and all aluminum-reduction plants in the world, except certain ones in Germany, consume electric energy derived from hydroelectric power plants. For this reason aluminum-reduction plants are normally situated within easy access of waterfalls, and steam-raised electric power is totally out of the question as a source of current for economical aluminum production.

**Preparation of Alumina.**—In the present Hall-Héroult process, the raw materials for the production of aluminum include substantially pure alumina, cryolite (plus calcium and aluminum fluorides for the bath), and carbon electrodes, and the first step in the manufacture of the metal consists in the purification of bauxite by chemical methods, whereby substantially pure alumina is produced. There are two main processes for the preparation of alumina, although many patents have been taken out for doing this in one way or another. These processes are (1) the Bayer process, and (2) the Deville-Pechiney process. The preparation of alumina has been discussed at length in the literature.<sup>3,8,12,18-44,45</sup>

The usual process employed for the preparation of alumina from bauxite is the Bayer process, a wet chemical method. In this, the chemical principle involved is the formation of sodium aluminate by the treatment of bauxite with aqueous sodium hydroxide and the subsequent precipitation of aluminum hydroxide from the sodium aluminate, followed by calcination of the aluminum hydroxide to alumina ( $\text{Al}_2\text{O}_3$ ). In practice, calcined bauxite is first ground, *e.g.*, in a ball mill, to 100 mesh or finer, and this is next mixed with aqueous sodium hydroxide, specific gravity 1.45 (44.8°Be'). in a vessel fitted with stirrers. After intimate stirring, the mixture is then run into steam-jacketed autoclaves and digested for 2 to 8 hr. under 50 to 70 lb. pressure at 150 to 160°C. The alumina of the bauxite is acted upon by the sodium hydroxide with the formation of sodium aluminate, according to



The impurities ferric oxide and titania are unaffected by the sodium hydroxide, as is the greater part of the silica. Part of the silica is dissolved and reacts with alumina and sodium oxide to form insoluble double aluminum sodium silicate. Dissolution of silica is prevented by adding lime to the bauxite during fine grinding, and this subsequently causes the formation of insoluble calcium silicate and prevents loss of alumina. About 90 per cent of the alumina in the bauxite is dissolved by the digesting treatment.

When the digesting treatment is completed, the liquor (including the residue of impurities) from the autoclaves is blown into large iron settling tanks of about 1,600-cu. ft. capacity and allowed to settle for 4 to 5 hr. so as to effect separation of the solid impurities. The settled residue contains ferric oxide, silica, titania, and other impurities from the bauxite, as well as some alumina not dissolved, and is known as "red

mud." This is discarded. The sodium aluminate liquor from the autoclaves is first diluted from specific gravity 1.45 to 1.23 (26.9°Be'), and after settling in the tanks is run through filter presses for removing suspended matter and into large precipitation tanks or decomposing vessels. Figure 6 shows a type of tank fitted with stirring apparatus used by European producers<sup>44</sup> for precipitation of aluminum hydroxide. In precipitating aluminum hydroxide from the sodium-aluminate liquor, a small amount of freshly prepared aluminum hydroxide is added to the tank and the whole is stirred; aluminum hydroxide is precipitated from the liquor over a period of time running up to about 60 hr. About 70 per cent is precipitated in 36 hr., and the remainder precipitates on further standing. The precipitated aluminum hydroxide settles to the bottom of the tank, where it is drawn off and put through filter presses, yielding a product for calcination to alumina. The sodium-hydroxide liquor from the tanks is evaporated in vacuum pans and concentrated to specific gravity 1.45 for reuse in the treatment of raw bauxite.

After filter pressing, the partially dried aluminum hydroxide is calcined so as to drive off water and yield substantially pure alumina. This calcination is generally

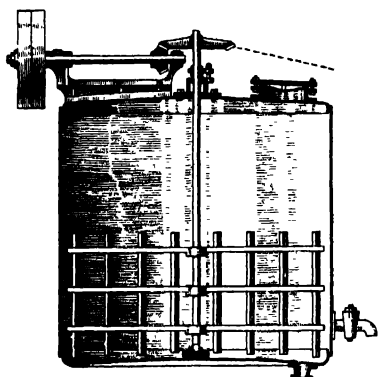
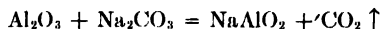


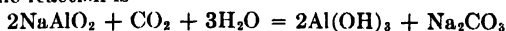
FIG. 6.—Bayer precipitation tank.

carried out in tubular rotary kilns, lined with fire brick, and similar to those used in calcining bauxite or burning cement. The kilns are run at 1000 to 1100°C. The resulting alumina contains 98 to 99.5 per cent  $\text{Al}_2\text{O}_3$ , and may contain up to 0.30 per cent mechanical water, 0.50 per cent combined water, 0.20 per cent silica, 0.10 per cent ferric oxide, and other impurities in subordinate amounts. After calcination, the alumina is ready for use in the electrolytic-reduction cell.

The Deville-Pechiney (or Le Chatelier-Morin) process was formerly the principal process for the preparation of alumina, but this has been largely supplanted by the Bayer process. The former is still used, however, for the treatment of bauxites especially high in iron, but it is not suitable where silica is high. In the process, ground bauxite, after calcination, is mixed with sodium carbonate, about 1 to 3 parts of sodium carbonate and 1 part bauxite, and the mixture is roasted in a rotary or reverberatory furnace for 2 to 4 hr. at 1000 to 1100°C. A small amount of powdered coal is sometimes added to the mix. The sodium carbonate combines with the alumina, carbon dioxide is evolved, and the impurities are unattacked. The roasting must be done with care to avoid melting of the mix, and the product of the roast is a grayish-brown substance, consisting of a mixture of sodium aluminate and the impurities. The reaction is



After roasting, the mass is lixiviated with hot water, whereby the sodium aluminate is dissolved, while the silica, ferric oxide, and titania, being insoluble, are left as a residue. The liquor is settled for the removal of the solid impurities, as in the Bayer process, and is then passed through filter presses, for removal of any suspended matter, and then into tall precipitation tanks. For precipitation, carbon dioxide is blown into the liquor, and the reaction is

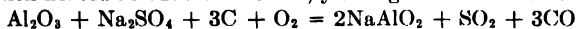


This precipitation requires 4 to 5 hr. and is carried out at 70°C. The precipitated aluminum hydroxide is filter pressed, dried, and calcined, as in the Bayer process, yielding alumina.



Some other processes have been devised and actually employed for the preparation of alumina, but only one, *i.e.*, the sulphuric acid process for the treatment of high-silica bauxites, is in commercial use at the present time. Certain other methods for obtaining a compound of aluminum (such as the fluoride, nitride, carbide, and chloride) from aluminum minerals have been worked out. A few of these possess potentialities, but the majority of them have no discernible commercial possibilities. While many processes have been devised for the preparation of alumina from clays and other fairly high aluminous minerals, none of these is commercial. There is very great need for a cheap process which will successfully accomplish this, thereby reducing the cost of aluminum. A few processes which have been employed commercially or have reached the semicommercial scale are discussed briefly below.

In the sulphuric-acid process for the treatment of high-silica bauxites, the ore is first ground finely, heated, and then treated with warm sulphuric acid, specific gravity 1.25, with the formation of aluminum sulphate. Separation is made from the impurities, the solution evaporated, and the salt calcined to alumina. In the Peniakoff process, ground bauxite, sodium sulphate, and a small amount of coal are mixed, and the mix then heated at 1200 to 1400°C., yielding sodium aluminate, according to



The sintered mass is then treated as in the Deville-Pechiney process for the production of alumina. In the Serpek process, aluminum nitride is produced by heating a mixture of ground crude bauxite and carbon in an atmosphere of nitrogen at 1600 to 1800°C. The aluminum nitride formed may be roasted with sodium carbonate yielding sodium aluminate and ammonia, or it may be decomposed by the action of water to form aluminum hydroxide and ammonia, according to



Further treatment in either case is as in the Bayer process. Other processes have been devised by Tone, Sinding-Larsen, Cowles,<sup>1</sup> Childs, Leccesne, Schwan, Miguet, Haglund and others, but these cannot be discussed here.

**Primary Aluminum Manufacture.**--The present commercial process for the production of aluminum is essentially the same as that described in the original Hall-Héroult patents of 1886 to 1888, and all aluminum made today is produced by the electrolytic dissociation of alumina dissolved in a bath of liquid (fused) cryolite plus other added salts. The sodium-reduction process need not be considered here, since it is largely of historical interest, but it is important to direct attention to the Cowles alloy process, since this may again find commercial application in the production of light aluminum alloys directly from ores. It should be pointed out that, although Hall applied for his patents in 1886, these were not granted until 1889, and in 1886 Héroult also applied for a United States patent on essentially the same process as described by Hall. The essential differences in the patent applications were in the composition of the electrolyte and the design of the furnace, but the two processes are identical to all intents and purposes. When the separate discoveries of Hall and Héroult were made simultaneously, there was no patent litigation, but the Hall company took the American field and the Héroult company the European field.

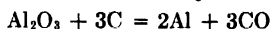
The Cowles process<sup>19</sup> for the manufacture of aluminum alloys directly from ores was patented by A. H. and E. H. Cowles<sup>2</sup> in 1885, and plants for conducting the process were built at Lockport, N. Y., and Stoke-on-Trent, England. In essence, the Cowles process called for the reduction of alumina by carbon in the presence of a metal (*e.g.*, copper) in the heat of the electric arc. While alumina can be reduced by carbon,

<sup>1</sup> U. S. Patents 1040892, 1040893; 1040894, 1040895, and 1040897, all dated Oct. 8, 1914.

<sup>2</sup> U. S. Patents 324658 and 324659, Aug. 18, 1885; and foreign patents.

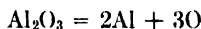
as pointed out previously, the metal so reduced will either combine with the carbon, forming aluminum carbide; combine with carbon monoxide or dioxide, forming aluminum carbide or oxide; combine with any oxygen present; or else volatilize. In the presence of another metal, however, say copper or iron, the reduced aluminum alloys with the other metal, thereby forming an intermediate alloy. In the Cowles process, when copper is used, alloys containing 15 to 40 per cent aluminum and the remainder copper are produced, and these were diluted with copper in making aluminum bronze.

In the process, a correctly proportioned mixture of alumina, carbon, and copper is placed in an electric-arc furnace and smelted. Copper, or any other metal used for alloying, has no effect upon the actual reaction, since what takes place is simple reduction of alumina by carbon at elevated temperatures, according to



During the years 1885 to 1890, the alloys made by the Cowles process could be produced at a lower price per pound of contained aluminum than substantially pure aluminum itself, and as a consequence a considerable measure of success was had. The process is now obsolete, but it may become an economic possibility in the future to produce certain intermediate or light aluminum alloys by direct reduction from ores, involving this or a similar method.

**Hall Aluminum Process.**—In 1886, C. M. Hall, of Oberlin, Ohio, found<sup>1</sup> that alumina dissolved in a liquid (fused) solution of aluminum fluoride and another metal fluoride, *e.g.*, sodium, formed an electrolyte, and that the alumina could be dissociated by the electric current, according to



The electrometallurgical principle involved in the process, then, is the electrolytic decomposition of alumina dissolved in a bath of fused fluorides of aluminum and other bases; the current causes dissociation of the alumina into aluminum and oxygen without appreciably affecting the solvent. This invention caused a revolution in the aluminum industry. It should be added that C. S. Bradley applied for a patent covering the electrolytic dissociation of aluminum compounds in 1883, but this patent was not granted<sup>2</sup> until 1892. This Bradley patent was the cause of litigation first between the Electric Smelting and Aluminum Co. (*i.e.*, the Cowles company) and Paul Héroult regarding title to it, and second between the Cowles company and the former Pittsburgh Reduction Co. (*i.e.*, the present Aluminum Co. of America). Title to the Bradley patent was awarded to the Cowles company, and after long litigation it was decided by the courts that the Pittsburgh Reduction Co. in using the Hall patents had infringed the Bradley patent.

In development of the Hall process, it was found that cryolite made a good solvent for alumina, and cryolite, as such, or plus calcium and aluminum fluorides, is employed for the electrolytic bath in present practice. In the process, the aluminum is liberated and sinks to the cathode, while the oxygen goes to the anode, which it attacks, burning to carbon monoxide and finally to carbon dioxide on contact with the air. The electrolysis is carried out in a carbon-lined furnace or cell, the carbon lining serving as the cathode and separate carbon electrodes as the anodes. In the Hall reduction cell, the electric current serves two important functions; *viz.*: (1) it keeps the electrolytic bath liquid by the generation of heat, and (2) it causes electrolytic dissociation of the

<sup>1</sup> U. S. Patents 400664, 400665, 400666, 400667, and 400766, Apr. 2, 1889.

<sup>2</sup> U. S. Patent 468148, Feb. 2, 1892.

alumina. Theoretically, the decomposition voltage required is 2.8, but in practice about three times this is actually used.

As indicated, P. L. V. Héroult, of Paris, France, brought out a process in 1886 for the preparation of aluminum by the electrolysis of alumina dissolved in cryolite, and this process is identical in principle with that of Hall. Héroult's first patent<sup>1</sup> called for the preparation of aluminum and aluminum alloys by the electrolysis of alumina dissolved in cryolite, and in making aluminum alloys a negative electrode of the metal to be alloyed was employed. This method was never applied commercially to the production of alloys, but it was used for aluminum. In Héroult's<sup>2</sup> second method, a process for making aluminum alloys was specified, in which alumina was melted by the electric current and electrolyzed by the same current, using a liquid metal, *e.g.*, copper, beneath the aluminum as the cathode. The resulting product is an intermediate alloy of aluminum and copper, similar to that obtained by the Cowles process. Alumina, without copper or another metal present, cannot be electrolyzed to produce aluminum, since the metal would be volatilized at the temperature prevailing. This process was operated for a short time at Neuhausen, Switzerland, but was abandoned in 1891, and the production of aluminum taken up in accordance with Héroult's first patent.

Many methods have been devised for the production of aluminum both before and since the invention of the Hall-Héroult process, but all aluminum made now is produced by this process. The older methods have been discussed at length in the books by Richards<sup>3</sup> and Minet<sup>4</sup> and need not be considered here, but it is of interest to touch briefly upon some processes that have been devised in recent years. However, none of these is now commercial.

A method for the production of aluminum directly from aluminum-bearing minerals has been patented by Tone,<sup>5</sup> in which aluminum ore is smelted to aluminum carbide with carbon in an electric furnace, and this is then mixed with silica and smelted to an aluminum-silicon alloy or with aluminum oxide and smelted to aluminum. The process is uneconomic, even if it is technically sound. Betts<sup>4</sup> has patented a process entailing the smelting of kaolin in a blast furnace to an iron-aluminum-silicon alloy. This alloy is then oxidized, sulphurized, or chloridized to aluminum oxide, sulphide, or chloride, and in the sulphide the compound is electrolyzed to aluminum and sulphur. In a patent by Kiscock,<sup>5</sup> an aluminum-silicate mineral is smelted with carbon to aluminum carbide, and this is converted to aluminum sulphide. The latter is electrolyzed in a suitable bath. Many carbon-smelting processes for the direct reduction of aluminum have been devised, but, as stated, these are all technically unsound. A number of patented processes call for the electrolysis of aluminum salts in aqueous solution, but these are unsound.

The fundamental principle of the Hall-Héroult process is the electrolytic dissociation of alumina dissolved in a bath of aluminum fluoride and the fluoride of one or more metals more electropositive than aluminum, *e.g.*, sodium, potassium, or calcium. The composition of the electrolytic bath is especially important, and this will be discussed briefly. Both natural and artificial cryolite are used as the base in making up baths, and the actual bath composition may vary over a fairly wide range. Cryolite melts at 995°C., and the eutectic mixture 81.5:18.5 cryolite-alumina melts at 935°C. By the addition of various salts, the melting point may be reduced to 700°C. The specific gravity of the liquid bath must be less than that of liquid aluminum at the operating temperature, since otherwise the dissociated metal would rise, instead of sink, and upset the cell. A typical bath contains 66.8 per cent aluminum fluoride

<sup>1</sup> French Patent 173711, Apr. 23, 1886.

<sup>2</sup> French 170003, Apr. 15, 1887; and U. S. Patent 387876, Aug. 14, 1888; and other patents.

<sup>3</sup> U. S. Patent 961913, June 21, 1910.

<sup>4</sup> U. S. Patent 938634, Nov. 2, 1909.

<sup>5</sup> U. S. Pat. 1052727, Feb. 11, 1913.

and 33.2 per cent sodium fluoride. In the Hall process, the following composition has been employed for the bath; 59 per cent aluminum fluoride, 21 per cent sodium fluoride, and 20 per cent calcium fluoride. This bath dissolves 20 per cent alumina at the operating temperature. Cryolite has a specific gravity of 2.92 in the solid state and of 2.08 in the liquid state, while aluminum has a specific gravity of 2.70 in the solid state and 2.31 in the liquid state (at 900°C.). Hence at the operating temperature, the metal collects at the bottom of the bath.

The e.m.f. required for dissociation of the alumina in the process is 2.8 volts, but in practice at least three times this is necessary because of the resistance of the bath and connections and small losses here and there in the circuit. In general, irrespective of the type of furnace, each unit requires 6.5 to 7.5 volts for operation, and, in starting, a wider range, 5.5 to 8.5 volts, is necessary. It is not yet economical to build dynamo-generators of such low voltage, and consequently thirty to forty furnaces are connected in series; thus, the operating voltage for thirty-five furnaces would be 250 volts. The

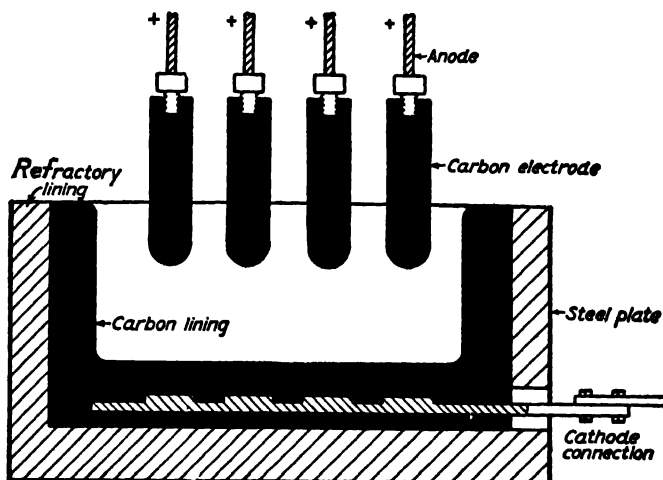


FIG. 7.—Aluminum reduction cell.

current density varies over a rather wide range, *e.g.*, 1.5 to 3 amp. per square centimeter in certain French furnaces, and 650 to 750 amp. per square foot in some American cells. The current employed depends upon the size and the number of electrodes—8,000 to 10,000-amp. lines are common, and there are larger furnaces using 15,000 to 20,000 amp. Theoretically, there should be 0.33912 g. of aluminum produced per ampere-hour, or 0.7476 lb. per 1,000 amp.-hr. The theoretical anode consumption is 0.67 lb. per pound of aluminum produced, but in practice this amounts to 0.8 to 1.0 lb. The consumption of alumina per pound of aluminum produced is about 2 lb. in practice—1.888 lb. theoretically—and about 0.1 lb. of cryolite or bath material is consumed.

As mentioned in a later paragraph (*cf.* Commercial Aluminum, below), the product of the Hall-Héroult reduction cell is not pure aluminum but contains appreciable amounts of impurities. Many attempts have been made to refine impure aluminum and to produce *pure* metal, but this had not been accomplished until recently when the Hoopes process was developed. The method is described in patents<sup>1</sup> granted to

<sup>1</sup> French Patents 575463, 575464, 575465, 575466, and 575467, all dated 1924; British Patents 223388 and 225494, Dec 20, 1923, and 224488, Nov 5, 1923; and U. S. Patents 1534315 to 1534322 inclusive, April 21, 1925; and other patents.

Hoores and others and owned by the Aluminum Co. of America. Detailed discussion of the process cannot be given here, but very briefly a cell is employed in which there are three horizontal layers; the lowest layer is a liquid aluminum-copper alloy anode, above this is a layer of fused cryolite-barium fluoride solution (the bath electrolyte), and floating on top is the cathode of pure liquid aluminum. The cell operates at about 6 volts and 20,000 amperes. Cathode metal containing as high as 99.98 per cent Al has been produced in the Hoopes cell in regular operation. The mechanical, physical, and chemical properties of *pure* aluminum are markedly different from those of the ordinary 99+ per cent commercial metal.

**Aluminum-reduction Furnaces.**—All furnaces now in use for the electrolytic production of aluminum, other than the Hoopes cell, are essentially the same in general design, although they vary considerably in constructional detail. The usual furnace consists of a rectangular box of mild steel lined with a refractory material of low thermal and electrical conductivity, and within this a heavier lining of rammed carbon forming the cathode. This carbon lining is made of petroleum coke with a suitable oil or tar binder rammed in place; plates of iron may be molded in the bottom to form the cathode connection. In some furnaces, the lining is made as a separate unit, which is molded and baked similar to the anodes. There is great advantage in this type of lining, since a furnace that becomes inoperative can be renewed with a minimum of labor by simply removing the old lining and replacing it with a new unit. Figure 7 shows the general lines of the modern Hall-Héroult furnace with the anodes. In some furnaces, electrodes of carbon are embedded in the bottom of the furnace.

In all types of furnaces, the bottom is inclined towards the tap hole, and each anode is arranged so that it can be operated independently of the others. Aluminum furnaces are built in various sizes, *e.g.*, 8 ft. long by 4 to 5 ft. wide by 2 ft. high, and generally rectangular shapes are now in use in place of the former round cells.

A set of anodes is suspended in the interior of each furnace, and these vary in size and length. Anodes are round, square, and rectangular in section, from 3 to 16 in. in diameter or width, and the length varies from 8- to 40-in. Anodes are suspended in the bath in groups of from eight to twelve, and are closely grouped. They are clamped to a heavy frame support by suitable connections so that the group as a whole, or each individual anode, can be raised or lowered mechanically for control of the current and to insure equal distribution. Various types of furnaces have been described by Nissen.<sup>44</sup>

In the operation of a typical furnace, in starting, the bottom is first covered with granulated carbon shoveled in loosely, the anodes are then lowered to make contact therewith, and the current thrown on. As the furnace heats, cryolite or a prepared bath material is added. This melts, and the anodes are raised with an increase in the bath volume, and more cryolite is added until the furnace is full. When the bath is carrying the requisite current, alumina is charged in small amounts at a time until the furnace is in full operation. Of course, other salt additions are made to the bath during the starting operation, *e.g.*, calcium fluoride and aluminum fluoride, depending upon the bath employed. Alumina is added until the bath contains 10 to 20 per cent  $Al_2O_3$  in solution. On electrolysis, the aluminum sinks and collects on the cathode bottom, from whence it is tapped periodically, and the oxygen liberated at the anode interacts therewith. In operation, the alumina content of the bath is controlled by voltmeters and incandescent lamps connected across the terminals. When the alumina content becomes low, the furnace voltage rises from the normal

7 volts to 15 to 20 volts. The lamps are so connected that when the bath reaches a certain resistance they light, thus giving notice to the operator.

Every two or three days, according to the capacity of the furnace, the liquid aluminum is run off through a tap hole in the side. This metal is remelted in order to remove occluded bath salts and is then cast into pigs, forming the primary aluminum of commerce. First-grade aluminum contains 99 to 99.5 per cent Al (by difference). The cost of production of aluminum is now 13 to 15 cts. per lb. depending upon conditions.

**Manufacture of Carbon Electrodes.**—Since the anodes come into direct contact with the bath, they must be as free as possible from impurities, particularly iron and silica, *i.e.*, the ash content must be extremely low, and the manufacture of anodes is an important part of modern aluminum production. Petroleum coke is the best material for anode manufacture, and in practice the coke is first crushed to small nut size and then calcined for three or four hours at a red heat in a calcining furnace, *e.g.*, one of the Meisser type. After cooling, the calcined coke is ground, usually with waste electrodes, in a ball mill, to pass 16 to 18 mesh, of which 40 per cent passes 100 mesh. The ground coke is next mixed with a binder of pitch, or tar and oil, in steam-jacketed kneading machines, and then transferred to electrode molds or presses. The usual press is hydraulic in operation, and pressures up to 500 atmospheres are used.

After the electrode shapes have been formed in a press, they are air dried and then baked in a furnace or kiln in order to remove the volatile binder. The temperature of baking is 1000 to 1400°C., depending upon the size and binder, and the heating is done slowly in order to avoid cracking. Several days are required for firing the largest sizes of electrodes. The temperature is gradually raised during the operation, and the electrodes lose about 10 per cent in weight. The furnaces are generally fired with producer gas, and the electrodes are placed in refractory saggars packed with retort-carbon powder, ground petroleum coke, or electrode scrap. Many types of furnaces are employed in baking, the common ones being the Mendheim tunnel furnace and the Meisser chamber furnace. The apparent density of petroleum-coke electrodes is 1.55 to 1.70, the real density is 1.95 to 2.05, and the ash content less than 0.3 per cent. Finished electrodes should have an electrical resistivity of about 0.0016 ohm. The production of electrodes and the apparatus used have been treated in detail by Nissen.<sup>44</sup> The Söderberg continuous electrode has been tried in aluminum furnaces.

**Commercial Aluminum.**—The product of the reduction cell, after remelting, appears on the market as primary aluminum, and this is graded according to the amount of impurities present. The chief impurities are iron, silicon, copper, and alumina, while carbides, sulphides, sodium, nitrogen, and titanium are normally present in very small amounts. Ordinarily, three grades of primary aluminum are marketed; *viz.*, (1) special, containing 99.5+ per cent aluminum (by difference); (2) grade No. 1 (or grade A), containing 99+ per cent aluminum; and (3) grade No. 2 (or grade B), containing 98 to 99 per cent aluminum. Primary aluminum alloys are prepared by a remelting operation in which an alloying metal is added to primary aluminum. In practice, the quality of aluminum is ordinarily based on a chemical analysis in which copper, iron, and silicon are determined, and the remainder is said to be aluminum. Some method of analysis for the direct determination of aluminum should be employed. In

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99+ per cent aluminum, the content of impurities is usually; copper, trace to 0.20; iron, 0.25 to 0.60; and silicon, 0.15 to 0.40 per cent. Alumina ( $\text{Al}_2\text{O}_3$ ) is a normal impurity in commercial aluminum.

Primary aluminum pig appears on the market in different forms which vary among producers. Thus, there are large three-notch pigs, which are about 3 ft. long and weigh about 33 lb., and small notch bars with six to ten notches, weighing 3 to 10 lb. The form of the standard 3-lb. notch pig made by the British Aluminium Co., Ltd., is shown in Fig. 8. Some foreign pig is poured into waffle molds, yielding 3-in. square plaques about 1 in. thick, joined by thin webs. Aluminum pig is known variously in the trade as aluminum ingot, notch bar, etc. Aluminum rolling ingots, blocks, and slabs are furnished by producers for rolling and other working. Specifications for aluminum pig have been worked out by the U. S. Army Air Service, the French Aeronautical Board, the British Engineering Standards Association, and the A. S. T. M., among others.

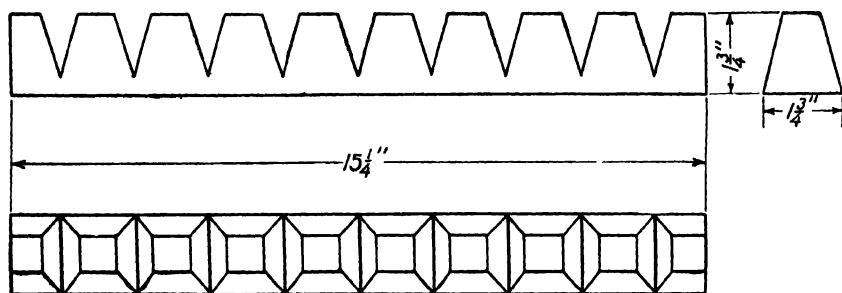
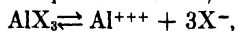


FIG. 8.—Aluminum ingot. (Brit. Al. Co., Ltd.)

**Chemical Properties of Aluminum.**—The chemical properties of aluminum are remarkable and of great importance. The chemical properties of the metal and its interactions with various substances have been ably discussed by Little<sup>10</sup> and Mellor<sup>17</sup> in their books, and these may be consulted for detailed information. Aluminum is very reactive chemically and under proper conditions combines readily with oxygen, the halogens, nitrogen, sulphur, and carbon; it is readily attacked by some acids, but not at all, or slightly, by others; and it is readily soluble in alkalis. The chemical properties of light aluminum alloys are, in general, similar to those of the substantially pure metal. Aluminum is a silvery-white metal with a slightly bluish tinge, and it has great coloring power, *i.e.*, it readily whitens colored metals in alloys. Aluminum forms one series of salts in which it is trivalent, and the salts are derived from the basic oxide,  $\text{Al}_2\text{O}_3$ . Aluminum salts are non-poisonous, and consequently aluminum cooking utensils are preferred to tinned steel utensils. On the basis of the ionic hypotheses, the salts of aluminum dissociate in aqueous solution, according to



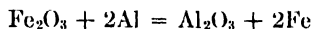
yielding the colorless cation  $\text{Al}^{+++}$ . The ionic mobility of the cation  $\frac{1}{3} \text{Al}^{+++}$  is 40.4 at 18°C., according to Heyweiller. Aluminum stands high in the electromotive series. The atomic weight of aluminum is now given as 26.97 by the International Union of Pure and Applied Chemistry.

**Interactions with Various Substances.**—A few of the principal interactions of aluminum with various substances are indicated briefly here, and further infor-

mation will be found below under Corrosion of Aluminum and Aluminum Alloys, particularly on the action of air and water. Aluminum is attacked slowly by cold acetic acid, but the rate of attack increases markedly with increasing temperature and increasing dilution of the acid. Butyric acid attacks aluminum slightly in the cold, but with boiling butyric acid the action is similar to acetic acid. Aluminum is attacked very rapidly by hydrochloric and hydrofluoric acids in all concentrations, with the evolution of hydrogen. Lactic acid has very slight effect. Cold concentrated or dilute nitric acid attacks aluminum slowly, and the metal can be employed for handling such acid. Traces of sulphuric acid in nitric acid increase the rate of attack. Oleic acid has practically no effect on aluminum. Aluminum is dissolved appreciably by hot dilute sulphuric acid, but the action of the concentrated acid is slow. Alkali hydroxides attack aluminum and its light alloys rapidly.

Aluminum interacts with carbon at high temperature to form aluminum carbide ( $\text{Al}_4\text{C}_3$ ) and carbon monoxide and dioxide interact with it forming aluminum carbide or aluminum oxide and setting free carbon. Aluminum carbide is decomposed by water, yielding aluminum hydroxide and methane. Chlorine, bromine, and iodine all attack aluminum rapidly. Nitrogen combines directly with aluminum at moderate temperature (400 to 800°C.), forming aluminum nitride ( $\text{AlN}$ ). This is attacked by water, yielding aluminum hydroxide and ammonia. Aluminum reacts with elemental sulphur at moderately high temperature to form the sesquisulphide ( $\text{Al}_2\text{S}_3$ ); with phosphorus, to form a number of phosphides; and with arsenic, to form the compounds  $\text{AlAs}$  and  $\text{Al}_3\text{As}_2$ . Aluminum forms many chemical compounds, notably the alums, *e.g.*,  $\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ .

**Oxidation of Aluminum.**—The affinity of aluminum for oxygen is very great, and fine aluminum powder, or very thin foil, burns in the air, on ignition, with great violence. The thermit reduction of metallic oxides is based upon the high affinity of aluminum for oxygen. Thus, when aluminum powder is mixed with a finely divided metallic oxide and the mixture ignited, the reaction takes place with violence, yielding aluminum oxide and the metal of the metallic oxide reduced, *e.g.*,



The molecular heat of formation of  $\text{Al}_2\text{O}_3$  is about 386,000 cal., or about 128,700 cal. per gram-atom.

Metallic aluminum is normally covered with a thin film of aluminum oxide, and when heated in air, at temperatures up to the melting point, small particles of aluminum are gradually oxidized to aluminum oxide. Much experimental attention has been given to the oxidation of aluminum, but considerable uncertainty still exists as to the actual final end product of oxidation. Thus, several oxides, other than  $\text{Al}_2\text{O}_3$ , are mentioned in the literature. Pionchon claims that the final end product of oxidation is  $\text{Al}_2\text{O}_3 \cdot 3\text{Al}_2\text{O}_3$ , indicating the existence of the suboxide  $\text{Al}_2\text{O}$ . Kohn-Abrest mentions  $\text{AlO}$ , and  $\text{Al}_4\text{O}_3$  and  $\text{Al}_6\text{O}_7$  have been described. All these seem unlikely. Rhodin, however, submits that substantially pure aluminum burns in air to form  $\text{Al}_3\text{O}_4$ , just as iron burns to  $\text{Fe}_3\text{O}_4$ . Aluminum quickly oxidizes if the surface is rubbed with mercury, an arborescent growth of aluminum oxide rapidly forming all over the metal. This phenomenon is known as the activation of aluminum.

**Properties of Aluminum and Aluminum Alloys.**—The general physical and mechanical properties of substantially pure (commercial) aluminum have been



fairly well determined, but much testing work on the properties of the light alloys is still needed. The tensile strength of aluminum is low, and the substantially pure metal finds limited and special employment for engineering construction, being valued chiefly because of its low specific gravity, great ductility, high electrical and thermal conductivity, and resistance to atmospheric corrosion. Where it is desired to take advantage of the low specific gravity of the metal, however, but where considerable strength is required, it is necessary to employ aluminum alloys.

Some excellent aluminum alloys have been developed for particular purposes, and certain of these possess tensile strength exceeding that of mild steel and the specific tenacity of alloy steels. Aluminum is malleable and ductile in the cold and can be rolled into sheet, drawn into wire, stamped and spun, and otherwise worked both hot and cold. Both the metal and its alloys are hot short at high temperatures, and some of the alloys are cold short. In working, certain definite temperature ranges have been found most suitable for particular alloys. Aluminum is the only commercial

TABLE 6.—PHYSICAL, MECHANICAL, AND OTHER PROPERTIES OF ALUMINUM<sup>1</sup>

Property	Units for expression	Value
Specific gravity, 20°C	Grams per cubic centimeter	2.70 ±
Specific gravity, liquid, 800°C	Grams per cubic centimeter	2.343
Solidification shrinkage	Per cent	6.6
Melting point	Degrees Centigrade	658.7
Boiling point	Degrees Centigrade	1800 ± 50
Thermal expansivity	Increase in length per cent of length per degree Centigrade (0 to 100°C)	0.0002353
Thermal conductivity, at 18°C	Gram-calories per cubic centimeter per 1 degree Centigrade per second (c.g.s. units)	0.504
Latent heat of fusion	Gram-calories per gram	77
Latent heat of vaporization	Gram-calories per gram	2100
Specific heat	Gram-calories per degree Centigrade (18 to 100°C)	0.212
Vapor tension	At melting point in millimeters of mercury	$1.0 \times 10^{-4}$
Specific electrical resistance	Microhms per cubic centimeter at 20°C	2.82
Temperature coefficient of resistivity	Per degree Centigrade (20 to 100°C)	0.0039
Magnetic susceptibility	$H \times 10^6$ , at 18°C	+0.65
Hardness (cast)	Brinell (10 mm, 500 kg, 30 sec)	25
Hardness (cast)	Scleroscope { Magnifier hammer	5-6
	Universal hammer	4-5
Tensile strength (cast)	Pounds per square inch	12,000
Yield point (cast)	Pounds per square inch	8000
Elongation (cast)	Per cent	20
Reduction in area (cast)	Per cent	35
Modulus of elasticity (cast)	Pounds per square inch	10,000,000
Compressive strength (cast)	Pounds per square inch	60,000
Linear contraction 700 to 25°C	Per cent	1.68
Surface tension, 700°C	Dynes per centimeter	520
Heat of combustion to $Al_2O_3$	{ Calories per gram-atom	128,700
	{ Calories per gram-molecule	386,000
Heat of chlorination to $AlCl_3$	Calories per gram-molecule	108,000
Heat of sulphuration to $Al_2S_3$	Calories per gram-molecule	42,000
Electrolytic solution potential against calomel electrode	Volts	1.04
Atomic weight	O = 16	26.97

<sup>1</sup> Data collected from various sources.

## METALLURGY OF ALUMINUM AND ALUMINUM ALLOYS

metal now available in large quantities that can be used for making light alloys, and the high specific strengths of these materials make them of very great importance to the engineer.

The physical properties of aluminum and aluminum alloys are variable over a wide range depending upon the chemical composition, the physical condition, i.e., whether cast or worked, and the heat treatment. From the commercial point of view, the following properties of aluminum and aluminum alloys are of importance in particular applications: specific gravity; hardness; tensile properties at the ordinary and elevated temperatures; modulus of elasticity; compressive strength; resistance to alternating stresses and impact; thermal expansion; growth on heating; thermal conductivity; electrical conductivity; and others. To the foundrymen, the following properties of aluminum alloys are of importance from the point of view of easy casting: contraction in volume and linear contraction; fluidity and viscosity; surface tension; latent heat of fusion; melting points; and some of the other properties mentioned above. The general physical properties of aluminum have been well summarized in *Circ. 76* of the U. S. Bureau of Standards, and valuable data are to be found in the book by Grard.<sup>13</sup> The reports to the Alloys Research Committee of the Institution of Mechanical Engineers<sup>27, 31, 37, 66</sup> may be consulted for data on the physical properties of some aluminum alloys.

Table 6 gives a summary of the principal physical and mechanical properties of substantially pure aluminum; the figures may be compared with the corresponding properties for magnesium in the chapter on the Metallurgy of Magnesium and Magnesium Alloys in this work. Table 7 gives the average tensile properties of substan-

TABLE 7.—TENSILE PROPERTIES OF SUBSTANTIALLY PURE ALUMINUM<sup>1</sup>

Form	Yield point, pounds per square inch	Tensile strength, pounds per square inch	Elong- ation on a 2-in. length, per cent	Reduc- tion in area, per cent
Sand cast . . . . .	8,000- 9,000	11,000-13,000	15-25	30-40
Chill cast . . . . .	9,000-10,000	12,000-14,000	20-30	50-60
Sheet:				
Fully annealed . . . . .	8,000- 9,000	12,000-15,000	15-30	30-40
Half hard . . . . .	10,000-12,000	18,000-22,000	10-20	20-30
Hard (heavy reduction)...	12,000-25,000	22,000-35,000	2-10	5-20
12-gage (ordinary reduction) . . . . .	17,000	25,000	7	15
16-gage (ordinary reduction) . . . . .	20,000	28,000	5	10
20-gage (ordinary reduction) . . . . .	22,000	30,000	3	7
Bar, hard-drawn . . . . .	14,000-25,000	28,000-35,000	3-10	6-20
Wire:				
Hard-drawn . . . . .	14,000-33,000	22,000-55,000	1-10	2-20
40-mil . . . . .	23,000	31,000	3	6
80-mil . . . . .	20,000	28,000	5	10
120-mil . . . . .	16,000	25,000	7	15
200-mil . . . . .	14,000	22,000	10	20

<sup>1</sup> Approximate values, from various sources.

tially pure aluminum in various forms. The tensile properties of aluminum at elevated temperatures may be determined from the formula given by the Aluminum Co. of America, *viz.*,

$$S_t = 14,107 - 32.14t,$$

where  $t$  = the temperature of testing in degrees Centigrade (between 50 and 400°C.), and  $S_t$  = the tensile strength in pounds per square inch at the temperature  $t$ . The solidification shrinkage of aluminum is high—6.6 per cent.

**Physical and Mechanical Properties of Aluminum Alloys.**—The general physical and mechanical properties of the light aluminum alloys vary over a wide range, depending upon the composition and the condition. The extreme limits of specific gravity of the commercial alloys are about 2.4 and 3.3, and most commercial alloys have a specific gravity of under 3.0. The contraction in volume of most of the alloys is high, but less than that of aluminum, and the silicon-bearing alloys have the least contraction. Experiments by the writer<sup>106</sup> have shown that the linear contractions of forty alloys vary in the range 0.95 to 1.80 per cent. The melting points of the alloys range below that of aluminum down to about 575°C., the 92:8 aluminum-copper alloy melting at 636°C. While aluminum is very soft, it can be hardened greatly by alloying, and the Brinell hardness of the commercial alloys ranges from 25 to 125 (10 mm. 500 kg., 30 sec.).

The tensile strength of the light aluminum alloys varies greatly, when cast in sand, depending upon the chemical composition, and, roughly, it lies between about 14,000 and 38,000 lb. per square inch. Chill-cast alloys are considerably superior as to strength and ductility than sand-cast ones. In castings, the strength is a function of the size of section and the pouring temperature, being less with increase of section size and increase of pouring temperature. Gillett<sup>34</sup> has shown that the strength of alloys poured at high temperatures may be 10 to 20 per cent less than when poured at low temperatures. The mechanical properties of most of the light alloys are improved by either hot or cold working, and the best properties of one class of alloys (duralumin) are brought out only by working followed by heat treatment and aging. Duralumin manufactures have been made with tensile strength up to 80,000 lb. per square inch. The elongation of sand-cast aluminum alloys varies from *nil* to around 12 per cent. Table 8 gives the tensile and other properties for some sand-cast aluminum alloys poured at low temperature.

Few data are available as to the compressive strength of aluminum alloys, but the range is roughly 70,000 to 100,000 lb. per square inch. At elevated temperatures, the alloys lose strength, and most are weak above 300°C. The addition of small amounts of iron, manganese, or nickel to binary aluminum-copper alloys increases their strength at high temperatures. All the aluminum alloys are exceedingly hot short, *i.e.*, weak at temperatures immediately below the solidus. In fatigue (resistance to alternating stresses) the behavior of the alloys is variable, but the following alloys will withstand 10,000,000 reversals with 7,000-lb. maximum fiber stress: *viz.*, 92:8 aluminum copper; 2 to 3 per cent copper, 12 to 15 per cent zinc, and remainder aluminum; and 1.5 to 2 per cent copper, 1.5 to 2 per cent manganese, and remainder aluminum. Forged duralumin will stand 100,000,000 reversals (White-Souther) at 15,000-lb. maximum fiber stress. The Charpy impact resistance of aluminum alloys is 1 to 5 ft.-lb., notched bar, while the Izod value is 2 to 6 ft.-lb.

The coefficient of thermal expansion of the commercial light aluminum alloys varies between  $22 \times 10^{-6}$  and  $27 \times 10^{-6}$ , *e.g.*, that of the 88:12 aluminum-copper alloy is  $26.4 \times 10^{-6}$ , as compared with  $22.31 \times 10^{-6}$  for aluminum. When a light aluminum alloy is heated, it first expands, as do most metals and alloys. After

TABLE 8.—TENSILE AND OTHER PROPERTIES OF A SERIES OF SAND-CAST LIGHT ALUMINUM ALLOYS<sup>1</sup>

Nominal composition, elements, per cent				Elastic limit, pounds per square inch	Yield point, pounds per square inch	Tensile strength, pounds per square inch	Elongation on a 2-in length, per cent	Reduction in area, per cent	Specific gravity	Brinell hardness <sup>a</sup>	Melting point, degrees Centigrade	Linear contraction, inches per foot
Al	Cu	Other metals	Mg									
100		...		2,000	8,000	12,000	20	35	2.70	25	658.7	0.202
96	4	...		...	10,000	16,500	5	7	2.77	45	650	0.188
92	8	...		8,000	12,000	19,000	1.5	2	2.85	65	636	0.172
88	12	...		9,000	15,000	21,000	0.5	1	2.93	70	620	0.168
95		...	5		16,000	22,000	1.0	2	2.62	...	630	0.175
90		...	10		18,000	24,000	0.5	1	2.54	...	600	0.140
98		2 Mn		4,000	7,000	17,000	7	9	2.75	40	654	0.198
95		5 Si		3,000	6,000	18,000	4	5	2.67	40	620	0.160
90		10 Si		5,000	10,000	20,000	2	3	2.49	50	597	0.150
87 <sup>b</sup>		13 Si		5,000	12,000	28,000	8	12	2.64	60	605	0.142
90		10 Zn			10,000	19,000	8.5	10	2.74	60	645	0.189
80		20 Zn			20,000	27,000	1	2	3.06	70	622	0.167
67		33 Zn		15,000	20,000	33,000	Nil	Nil	3.33	...	600	0.152
97	2	1 Mn		...		20,000	10	15	2.80	...	649	0.198
82	3	15 Zn				28,000	2	3	3.00	85	625	0.171
89.5	7.5	1.5 Fe			12,000	22,000	1.5	1.5	2.85	65	635	0.168
		1.5 Zn										
93	4	3 Si		...	10,000	18,000	2.6	2.5	2.80	50		
88.2	10	1.5 Fe	0.3		11,000	22,000	0.5	1	2.90	90	...	0.168
92.5	4	1.5 Ni	2		12,000	25,000	2	1	2.80	70	...	0.164

<sup>1</sup> Data from various sources.<sup>a</sup> 10-mm. ball, 500 kg., 30 sec.<sup>b</sup> Modified alloy.

reaching about 250°C., however, the increase in size becomes quite rapid and continues for some time, even though the temperature remains constant. This is called permanent growth, since on cooling down the increase in size is not lost. All the light aluminum alloys have thermal conductivity less than that of aluminum, and, generally speaking, the greater the percentage of additive elements in an aluminum alloy the lower the thermal conductivity. Unlike cast iron, the thermal conductivity of the aluminum alloys increases with increasing temperature; that of cast iron decreases very slightly. Whereas the thermal conductivity of aluminum = 0.504, that of the light alloys varies in the range 0.25 to 0.48, *e.g.*, the thermal conductivity of the 88 : 12 aluminum-copper alloy is 0.382 at 100°C. The electrical conductivity of the aluminum alloys is lower than that of aluminum, the resistivity ranging up to 5.70 microhms per centimeter cube. The electrical resistivity of duralumin is 3.35 microhms per centimeter cube. A most exhaustive study of the electrical properties of numerous aluminum alloys is due to Broniewski.<sup>35</sup>

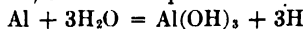
Many light aluminum alloys possess aging properties, *i.e.*, when freshly cast they may have their tensile properties enhanced by maturing at the ordinary temperature, and in the same way the machining properties may be improved. Thus, in foundry practice, it is usual to allow freshly cast parts of difficultly machineable alloys to age for some time at the ordinary temperature, when it will be found that they cut more satisfactorily than if machined soon after being taken out of the sand. In some alloys, the increase in tensile strength found on aging for one month after casting will be 25 to 30 per cent, but the elongation is decreased. The Brinell hardness increases on

aging at the ordinary temperature. Heat treatment enhances the strength and hardness of certain alloys most markedly.

**Corrosion of Aluminum and Aluminum Alloys.**—While it is often thought that aluminum and its light alloys are very susceptible to corrosion and that they, therefore, cannot be used for many purposes, these materials are actually more resistant to some corrosion influences, *e.g.*, ordinary atmospheric air, than are most simple steels. The behavior of the metal and its alloys in different corroding media is, of course, very variable, and the resistance to corrosion of different alloys in the same media may be, and usually is, variable. Thus, the corrosion of aluminum or any aluminum alloy may be rapid in an acid-gas atmosphere, but slow in sea water or in ordinary atmospheric air; also, an aluminum-zinc alloy may deteriorate rapidly in sea water, while an aluminum-manganese alloy will corrode slowly.

The greater resistance of aluminum and its light alloys to ordinary corroding media, as contrasted with iron and steel, is explained by the surface coating of aluminum oxide which forms and protects against further corrosion. The corrosion of aluminum is affected by its purity, and for applications where specific resistance against corroding media is desired, the purer varieties will withstand attack better than less pure metal. Thus, the 99.9+ per cent metal made in the Hoopes cell is practically not corroded at all in dilute hydrochloric acid, while the ordinary 99+ per cent metal is rapidly attacked. Some of the light aluminum alloys, and also aluminum, when worked, are subject to corrosion cracking (season cracking)—a phenomenon familiar to brass metallurgists—*i.e.*, the materials exfoliate and crack in certain solutions, owing to internal stresses. Hard-worked aluminum corrodes more rapidly than annealed metal in general, and cast aluminum corrodes more rapidly than the hard worked, because of minute pores in the former that give rise to local action. The corrosion of aluminum and its light alloys in various media has been described in many published papers, and only the more general aspects of the subject can be discussed here.

When aluminum and its light alloys are exposed to air, they become coated with a thin film consisting largely of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) or aluminum hydroxide in moist air. This film, if not broken down mechanically, serves as a protective coating, and apparently it should prevent further corrosion almost indefinitely. This film, however, may be broken readily by abrasion and other mechanical influences in service, and it is also penetrable by gases and liquids, so that it therefore does not serve as an effective protection unless it is fairly thick. Aluminum is attacked slowly by fairly pure atmospheric air and more rapidly by impure air. In ordinary damp air, the oxidation may be regarded rather more as an hydration of the metal taking place simultaneously with oxidation, since in the presence of moisture, the reaction



takes place and a colloidal film of aluminum hydroxide is formed. In the presence of carbon dioxide, the oxidation of the metal takes on a pitting effect, owing to the attack of carbon dioxide on the film of aluminum oxide and aluminum hydroxide, thus revealing a fresh surface of the metal to further action.

Aluminum is not attacked by distilled water, but is attacked by tap water, impure waters, and sea water, the corrosion depending upon the constitution of the waters. Oxygen is regarded as the prime cause of corrosion of aluminum by water. It has been indicated that alkalis attack the metal and its alloys rapidly, and alkaline waters are very corrosive. Aleoholic solutions and liquors have little action, and aluminum is used in the spirituous liquor and brewing industries for containers. So-called cutting solutions and compounds used for machining aluminum and its alloys have no effect

unless they contain soda ash or related sodium compounds. Ether has no corrosive action. Gasoline and oils have no action. Iron salts and compounds of iron cause a blackening of the metal. Lactic acid and milk have no action, and aluminum containers are used in dairying. Aluminum is attacked by some paints.

**Protection from Corrosion.**—Protective coatings may be applied to aluminum and its alloys for preventing corrosion, and enamels, paints, and varnishes are used. Spar varnish has been employed successfully for protecting aluminum and aluminum-alloy parts from sea-water corrosion on sea planes. Many patents have been secured for methods of coating aluminum, and the "browning" process of von Grotthuss may be mentioned. In this, the part is suspended in an electrolyte consisting of a sulphur compound of molybdenum with a zinc anode, at 60 to 65°C. The metal or alloy is soon covered with a dark-brown coating, and, according to the claims, can be bent or rolled without cracking the coating. Protected in this way, it is stated that aluminum has been immersed in salt solutions for two months without showing any traces of corrosion. Seligman and Williams, Röhrig, and others have found that the corrosion of aluminum in alkaline solutions is inhibited by the presence of sodium silicate in the solutions. A process (known as the Z-D process) has been worked out by Zimmerman and Daniels, at the McCook field plant of the U. S. Air Service, for treating aluminum and aluminum-alloy parts. This process is patented<sup>1</sup> and has been discussed by Zimmerman;<sup>133</sup> briefly, it involves treating parts to be protected with a solution of sodium silicate followed by baking. This treatment has proved efficacious in many cases and has wide application.

**Cracking and Disintegrating.**—There have been reports, at times, of certain strange cases of the cracking of aluminum alloys on standing, particularly in sand-cast aluminum-zinc alloys. Thus, it has been alleged that certain sand-cast parts of 88:12 aluminum-zinc alloy have cracked and finally completely disintegrated on standing in the storeroom.

Such allegations seem queer, and they do not seem to be supported by facts. Cracking in sand castings might be associated with shrinkage cracks and internal casting strains, but the light aluminum alloys are entirely permanent. Actual spontaneous disintegration of certain intermediate aluminum alloys does take place, however, and this has been observed many times in such alloys rich in iron, manganese, nickel, tin, cobalt, etc., but only in case relatively large proportions of both aluminum and the other metal are present in the alloy, *e.g.*, 50:50 aluminum-nickel. This behavior is, apparently, a property of certain definite compounds of aluminum with other metals, and these intermetallic compounds exhibit this behavior only when they constitute the whole, or nearly the whole, of the alloy.

**Commercial Aluminum Alloys.**—The subject of aluminum alloys opens up a wide field, and here it is possible to discuss only briefly those that find commercial application. Practice in the use of aluminum alloys is rapidly changing. Up to 10 years ago, only a few fairly definite alloys had had any large commercial employment, and these included certain binary aluminum-copper and aluminum-zinc alloys, certain ternary aluminum-copper-zinc alloys, and duralumin and its related alloys. The commercial casting alloys of aluminum have been recently discussed by the writer<sup>48, 141</sup>. Practice in the use of aluminum-casting alloys has changed radically from time to time. Thus, the aluminum-zinc alloys were

<sup>1</sup> U. S. Patent 1540766, June 9, 1925.

formerly used considerably in the United States for general castings, but these were later almost wholly supplanted by the aluminum-copper alloys. Both aluminum-zinc and aluminum-copper-zinc alloys are employed considerably in England. Recently, aluminum-silicon and aluminum-copper-silicon alloys have been developed for general casting, and the latter are to be the most promising alloys introduced for founding. Several special compositions have been developed for use in heat-treated sand castings, and with the further development of heat treatment it is expected that still more special and new alloys will be employed. In passing, attention should be drawn to the resourceful work of Daniels at the McCook field plant of the U. S. Air Service in developing heat-treatable casting alloys for aircraft parts. The so-called heavy alloys of aluminum, *i.e.*, aluminum bronzes and aluminum brasses, are relatively unimportant industrially due largely to difficulties experienced in casting.

In addition to the alloys already mentioned, some aluminum-magnesium, aluminum-manganese, aluminum-copper-iron, aluminum-copper-magnesium, aluminum-copper-manganese, aluminum-copper-nickel, and aluminum-copper-tin alloys are employed commercially. Some complex alloys are used in subordinate amount.

**Aluminum Casting Alloys.**—The bulk of the output of sand castings in the United States was formerly made in the standard 92:8 aluminum-copper (so-called

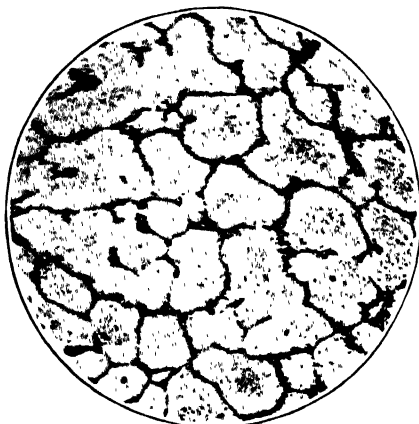


FIG. 9.—Sand cast No. 12 alloy; etched with NaOH ( $\times 75$ ).

No. 12) alloy. Thus, in 1919, of 81,000,000 lb. of sand castings produced here, 78,000,000 lb., or 97 per cent, was poured in 92:8 aluminum-copper alloy. Since then conditions have changed markedly, and in 1924 about 50 per cent of the sand castings made were produced in No. 12 alloy, 40 per cent in 90:7:1:2 aluminum-copper-iron-zinc alloy, and the remainder in other alloys. The use of both these alloys is decreasing, while that of the newer alloys is rapidly increasing. The principal report of investigations on the aluminum-copper alloys is that by Carpenter and Edwards,<sup>27</sup> and these alloys have also been discussed by the writer.<sup>72</sup> At the aluminum end, alloys containing 4 to 14 per cent copper are used for castings, but the alloy containing 7 to 8.5 per cent copper and the remainder aluminum is generally used. This is known in the trade as No. 12 alloy. In automo-

tive work, alloys containing 9 to 10.5 per cent copper and 11 to 13.5 per cent copper (and the remainder aluminum) have been developed for particular purposes, the former being used for pistons and the latter for manifolds. Commercial No. 12 alloy is not a simple binary alloy, but, in addition to copper, contains 0.5 to 1.5 per cent iron and 0.4 to 0.6 per cent silicon, and often manganese, nickel, zinc, tin, and other metals in subordinate amount. Figure 9 shows the microstructure of sand-cast No. 12 alloy. The 95:5 aluminum-copper alloy is used for general castings where more ductility is required than can be secured in the 92:8 aluminum-copper alloy. The light aluminum-copper alloys can be rolled up to 14 per cent copper. Certain intermediate alloys, *i.e.*, 33:67 and 50:50 copper-aluminum, are employed for making fixed additions of copper to aluminum and are known as "hardeners."

No binary aluminum-iron alloys are employed commercially, but some aluminum-magnesium alloys containing 4 to 10 per cent magnesium are used for sand castings. Some complex magnesium-bearing aluminum alloys are known as magaliums, and these are employed slightly for castings. These may contain 2 to 6 per cent magnesium, 1 to 3 per cent copper, and nickel and manganese in small amounts, but the compositions used are very variable. Some light aluminum-nickel alloys, *e.g.*, 94:6



Fig. 10.—93:4:3 Al:Cu:Si alloy. ( $\times 500$ , Dix.)

aluminum-nickel, were formerly used for sand castings. In 1920, aluminum-silicon alloys containing 5 to 15 per cent silicon were introduced by A. Pacz for general castings, and the 95:5 aluminum-silicon alloy is now employed extensively by the General Electric Co. for castings to be used in electrical manufacturing. It is important to state that the method used for preparing aluminum-silicon alloys has great effect upon their properties. When made simply by melting aluminum and silicon together, so-called "normal" alloys result. When the normal alloys are treated in the liquid state with an alkali fluoride flux, or if sodium or potassium be added, so-called "modified" alloys result. In the normal alloys, the silicon occurs as relatively large plates and needles, while in the modified ones the silicon is in a state of high dispersion. The aluminum-silicon alloys are known in Germany as "Silumin" and in France as "Aladar." The simple binary alloys are difficult to machine, and aluminum-copper-silicon alloys have been developed to overcome this objection, but still retain the good casting qualities of the binary alloys. The tensile strength of the normal alloys varies



from about 18,000 lb. for the 95:5 aluminum-silicon alloy to 21,000 lb. per square inch for the 87:13 aluminum-silicon alloy, and the corresponding elongation is 5 to 1 per cent. The modified 87:13 aluminum-silicon alloy has a tensile strength of up to 30,000 lb. and an elongation of 8 per cent.

Certain aluminum-tin alloys have been employed, and they yield white, strong, and ductile castings which polish and machine nicely, but tin is too expensive to use. In aluminum-zinc alloys, compositions in the range 5 to 35 per cent zinc and the remainder aluminum are employed, and zinc is the cheapest useful metal for alloying with aluminum. Such compositions as 95:5, 90:10, 85:15, 75:25, and 67:33 aluminum-zinc are common casting alloys. While suitable for sand castings, the alloys are useless for die casting. The principal report of investigations on these alloys is that by Rosenhain and Archbutt.<sup>47</sup> Most of the alloys can be readily worked, and all of them are excessively hot short and weak at elevated temperatures.

Turning to ternary and more complex alloys, certain aluminum-copper-iron alloys, *e.g.*, 90.5:8:1.5 aluminum-copper-iron, have been used for general castings, and it is known that the addition of small amounts of iron to the binary aluminum-copper alloys improves their mechanical properties. Light aluminum-copper-magnesium alloys are employed considerably in founding, and aluminum-copper-manganese alloys, *e.g.*, 97:2:1 and 95:3:2 aluminum-copper-manganese, have been used somewhat by particular manufacturers. These alloys are fairly strong and quite ductile, but their shrinkage is high. Light ternary aluminum-copper-nickel alloys were formerly used in the United States for sand casting, but this practice has been discontinued. However, certain of the alloys, *e.g.*, 90:8:2 aluminum-copper-nickel, are employed for die-casting and permanent-mold work. It is a fact that the substitution of 1 to 2 per cent nickel for copper in most aluminum-copper alloys gives better properties than can be obtained with copper alone. It has been pointed out that aluminum-copper-silicon alloys have been developed for sand casting, and alloys of the nominal compositions 87:3:10, 90:8:2, 91:6:3, 90:5:5, and 95:2.5:2.5 aluminum-copper-silicon are now used in practice. Apparently, the best alloys lie in the range of composition 3 to 5 per cent each of copper and silicon and the remainder aluminum. These alloys have good strength and ductility and excellent casting properties. Figure 10 shows the microstructure of the 93:4:3 aluminum-copper-silicon alloy. The 94:5:1 aluminum-copper-silicon alloy is used in the heat-treated condition for highly stressed parts subject to shock. Certain aluminum-copper-tin alloys are employed in a restricted way in founding. The presence of tin in aluminum-copper alloys seems to impart to the alloys capacity for taking a better polish. Two typical alloys used for sand castings are 90:8:2 and 85:5:10 aluminum-copper-tin.

Light alloys of aluminum, copper, and zinc are being employed to an increasing extent in the United States, and they are favored in England for many kinds of castings. The number of compositions used commercially is large, but several may be regarded now as reasonably standard. The alloys lie in the range of composition up to 10 per cent copper, up to 35 per cent zinc, and the remainder aluminum, and the most generally used alloy has the nominal composition 82:3:15 aluminum-copper-zinc, known in the trade as No. 31 alloy. The 83.75:2.75:13.5 aluminum-copper-zinc alloy is employed in England as a general casting alloy much in the same way that 92:8 aluminum-copper alloy is used in the United States. Other alloys employed in practice include 90:8:2, 90:5:5, 80:7:13, 72:3:25, and 65:3:32 aluminum-copper-zinc. In general, the alloys fall into two classes; *viz.*, (1) the high-zinc type, and (2) the low-zinc type. In both, the copper may be variable over a fairly wide range, but it is usually higher in the low-zinc alloys than in those high in zinc. Roughly, the high-zinc type includes alloys containing 20 to 25 per cent zinc and 3 to 5 per cent copper; the low-zinc type includes those up to 15 per cent zinc and 3 to 8 per cent copper.

A number of complex alloys are used for castings including 88.5:10:1.25:0.25 aluminum-copper-iron-magnesium (for parts subjected to elevated temperatures, *e.g.*, pistons), 95.5:2.5:1.5:0.5 aluminum-copper-iron-magnesium (for parts requiring good strength and ductility as cast), 89.5:2.5:1:7 aluminum-copper-iron-zinc (for general castings), and 92.5:4:1.5:2 aluminum-copper-magnesium-nickel (the so-called "Y" alloy of the National Physical Laboratory, used for parts requiring high strength as cast, for parts to be heat treated, and for high-temperature applications, notably pistons). Many alloys other than those indicated above have been tried and used in a small way, while numerous proprietary compositions have been exploited.

**Alloys for Working.**—Certain light aluminum alloys are suitable for rolling and forging, but at the present time the bulk of the production in wrought aluminum alloys is in duralumin and its related alloys. Duralumin, sometimes called duraluminum, in the commercial meaning of the term usually connotes the aluminum-copper-magnesium-manganese alloy composition developed by Wilm. More recently, it has been used as a generic word to connote low-copper heat-treatable alloys in general. The duralumin-type alloys are susceptible to heat

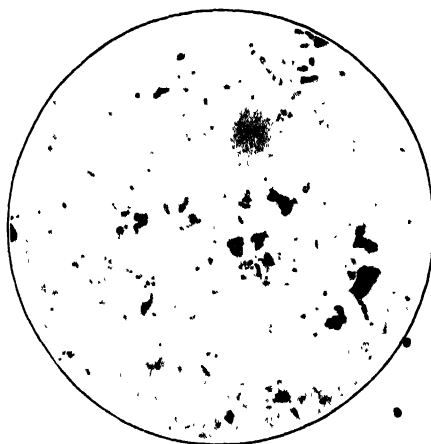


FIG. 11.—Duralumin sheet; water quenched from 512°C and air aged; etched  $\text{HNO}_3$  quench;  $\times 200$ .

treatment, some in greater degree than others, in that they harden on quenching followed by aging. There are known to be many alloys of different compositions that exhibit the duralumin phenomenon, and for convenience these may be divided into three classes, *viz.*, (1) ordinary or simple duralumin, (2) zinc duralumin, and (3) special duralumin. The ordinary duralumin is used largely at the present time, and the composition may be taken as

	PER CENT
Copper.....	3.5–4.5
Magnesium.....	0.5–1.0
Manganese.....	0.5–1.0
Aluminum (by difference) .....	remainder.

The usual impurities in aluminum, *i.e.*, iron and silicon, are also present, and it has lately been shown that the occurrence of silicon as an impurity in aluminum has been fortunate in the development of duralumin, since the effect of the inter-

metallic compound  $Mg_2Si$  upon the hardening of duralumin is most marked, as will be explained under the captions Metallography and Heat Treatment in later paragraphs.

The remarkable feature of duralumin and its related alloys is that they can be hardened very materially by quenching from 480 to 500°C., followed by aging at the ordinary temperature, and the aging may be accelerated by drawing at fairly low temperatures, *e.g.*, 100°C. for a short time. Worked duralumin, forgings and sheets, is now employed commercially for aircraft and motor-car construction in particular. The most remarkable recent development is the use of forged duralumin connecting rods on the Franklin and Hupmobile motor cars. Figure 11 shows the microstructure of a duralumin. The strength of duralumin is variable over a considerable range, the worked and heat-treated alloys ranging from 42,000 to 80,000 lb. per square inch tensile strength. Table 9 gives the mechanical properties of duralumin sheet in various forms. The tensile properties of forgings, bars, and wire are variable, depending upon the condition of the materials, as shown in Table 10. The properties and heat treat-

TABLE 9.—MECHANICAL PROPERTIES OF DURALUMIN SHEET IN DIFFERENT FORMS<sup>1</sup>

Property	Condition		
	Heat treated	Annealed	Hard rolled
Tensile strength, pounds per square inch	55,000-62,000	25,000-35,000	67,000-72,000
Yield point, pounds per square inch	30,000-36,000		55,000-65,000
Elongation on a 2-in. length, per cent	18-25	10-14	3-8
Brinell hardness	93-100	54-60	130-140
Scleroscope hardness	23-27	9-12	37-42

<sup>1</sup> Based on Knerr.

TABLE 10.—TENSILE PROPERTIES OF HEAT-TREATED DURALUMIN MANUFACTURES OF DIFFERENT KINDS

Material	Yield point, pounds per square inch	Tensile strength, pounds per square inch	Elongation on a 2-in. length, per cent
Bar stock:			
$\frac{1}{4}$ - to 1-in. diameter		55,000	18
1- to 1½-in. diameter		50,000	18
Over 1½-in. diameter		45,000	18
Forgings:			
Not over $\frac{3}{4}$ in. thick	30,000	55,000	18
Over $\frac{3}{4}$ in. thick		50,000	18
Wire	30,000-35,000	60,000-65,000	22-26

ment of duralumin have been discussed by a number of workers, including Thurston,<sup>63</sup> Merica and his collaborators,<sup>64</sup> Rosenhain and his co-workers,<sup>65</sup> Knerr,<sup>64</sup> and many others. The ordinary duralumins are not normally casting alloys, and, although they may be used to advantage for some castings, they have been employed principally in the form of rolled sheets, forgings, drawn and extruded rods, wire, and extruded tubes.

Zinc duralumin is a term used to connote a class of heat-treatable alloys of the composition, for example:

	PER CENT
Copper . . . . .	2 5
Magnesium . . . . .	0.5
Manganese . . . . .	0 5
Zinc . . . . .	20 0
Aluminum (by difference) . . . . .	remainder.

Zinc duralumins may be hardened by quenching followed by aging, as in simple duralumins. These alloys have been discussed by Rosenhain and his collaborators.<sup>65</sup> The tensile properties of the alloys after working and heat treatment are most remarkable. Rolled sheet, after quenching from 400°C. and reolling before hardening has set in, has the following properties; yield point, 64,000 lbs.; tensile strength, 75,000 lbs. per square inch; and elongation, 10 per cent. Of special duralumins, the 92.5:4:1.5:2 aluminum-copper-magnesium-nickel alloy has been considerably exploited, and the aluminum-magnesium silicide alloy (about 1 per cent magnesium plus sufficient silicon to form  $Mg_2Si$ ) developed as the result of investigations by Hanson and Gayler has had some use. This alloy is heat treatable, and is used for sheet, bars, rods, tubing, and special shapes. It is softer and less strong than ordinary duralumin, having strength of about 48,000 lbs. per square inch as rolled and heat treated as against 62,000 lbs. for duralumin. The 96:4 aluminum-copper alloy (with or without the addition of 0.5 per cent manganese) has found some use for sheet and shapes.

Referring to other aluminum alloys for working, certain aluminum-copper alloys, e.g., 2 to 4 per cent copper, are forged commercially, and the 98.5:1.5 aluminum-manganese alloy is employed considerably for rolling into sheet. This is known as "hard sheet aluminum." Schurmeister<sup>38</sup> has described extensive experiments on the rolling of various aluminum alloys. The 85:15 aluminum-zinc alloy is drawn for machining rod, and certain aluminum-copper-zinc alloys, e.g., 77:3:20 aluminum-copper-zinc is well adapted for rolling for the production of rods and shapes. The use of wrought aluminum alloys is just now being developed, but evidently forgings and sheet will ultimately be used extensively.

**Uses of Aluminum and Aluminum Alloys.**—A detailed recounting of all the uses and applications of aluminum and its alloys would require a volume of itself, and only the principal applications need be mentioned here. In a general way, aluminum has found useful application wherever low specific gravity, malleability, ductility, high thermal conductivity, high electrical conductivity, and resistance to corrosion are *desiderata*. Aluminum has been generally substituted for copper and the light alloys for brass and bronze in engineering work, and the metal and its alloys may be thus substituted wherever price is not prohibitive. About 50 per cent of the world's production of aluminum is used in the form of light alloys, principally castings, while 50 per cent is employed as substantially pure metal in the form of sheet, wire, bars, rods, tubes, and other finished and semifinished manufactures, and as foil, powder, and granulated aluminum. In the United States, about 40 per cent of the domestic output is consumed in the automotive industry, and for many years the status of aluminum production

in this country has been reflected fairly faithfully by the output of motor cars. Figure 12, showing the relation between the aluminum and automobile outputs in the United States over a period of years, may be noted in this connection.

The principal uses of aluminum may be summarized as follows: (1) as substantially pure metal in wrought and fabricated form, *i.e.*, as sheets, rods, wire, tubes, bars, molding, and special shapes; (2) in the form of light aluminum alloys for sand casting, die casting, permanent-mold casting, rolling, forging, extruding, and other working; (3) as aluminum powder in the aluminothermic process for the reduction of refractory oxides and the preparation of ferroalloys; (4) as aluminum powder in the aluminothermic (or thermit) welding process for repairing iron and steel parts; (5) as a deoxidizer in steel metallurgy; (6) as aluminum powder in calorizing, principally steel products; (7) as aluminum powder in the manufacture of explosives, *e.g.*, ammonal.

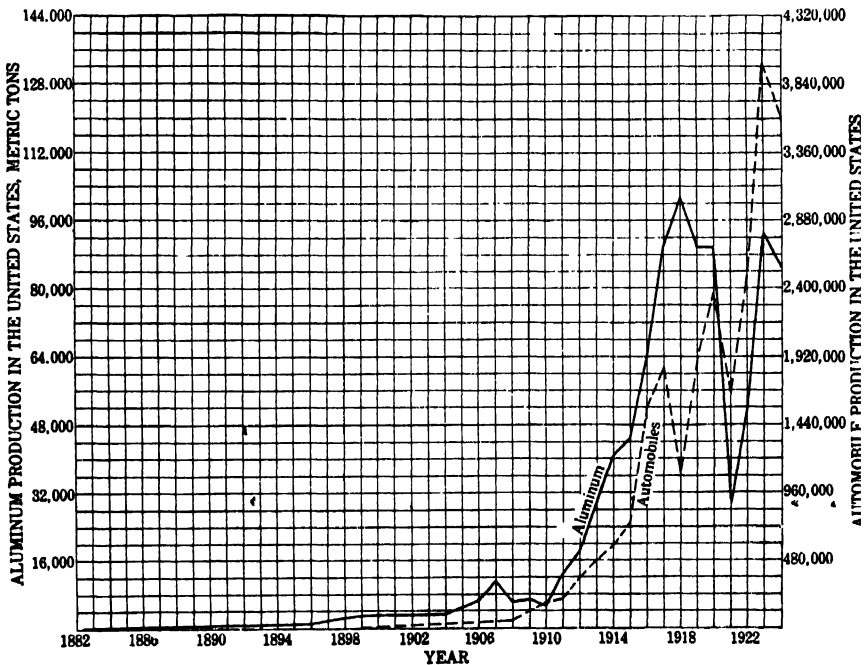


FIG. 12.—Relation between automobile production and aluminum consumption.

Some 200 commercial and technical uses of aluminum were listed by Richards in 1915, and an excellent account of the subject is given in papers by Guillet<sup>68</sup> *et al.*, written in connection with the French aluminum exposition in Paris in 1921.

The principal use of wrought or fabricated aluminum is in the form of sheet and wire. Aluminum sheet is employed extensively for paneling and body work for motor cars and aircraft; for the manufacture of spun and drawn kitchen cooking utensils; for vats, tanks, autoclaves, and special apparatus in the chemical industry; and a fairly large amount is used in the small stamping trade. Since aluminum sheet is very malleable and ductile in the cold, it can be spun, stamped, pressed, and drawn into any required shape, and its applications are almost limitless. Aluminum sheet is furnished in various gages from Nos. 10 to 40 Brown & Sharpe, and in various sizes up to 6 ft.

wide by 12 ft. long. Aluminum sheet, in addition to being used for automobile bodies, is employed for hoods, fenders, and small fittings, and gasoline tanks. It is also used extensively in aircraft, where it is practically indispensable for the fabrication of complicated cowlings, strut fairings, and other parts.

Substantially pure aluminum sheet is fabricated to make cooking utensils, and this has grown to be a large industry. A fairly large amount of aluminum is now employed for the production of vessels for the dairy industry and for vats, tanks, condensers, and other apparatus in the diversified chemical industry. In steel metallurgy, aluminum is used at most works as a deoxidizer in ingot production, and the addition of a small amount (1 to 8 oz. per ton) stops gas evolution and permits the production of sound ingots free from blowholes. Aluminum foil is simply very thin aluminum sheet, and is used extensively for wrapping tobacco, candy, and the like. Embossed, colored, and printed foil is produced. Aluminum bars, rods, tubes, molding, and special shapes are produced by drawing or extruding, and aluminum rivets are made in a variety of forms. Bars are employed for electrical conductors, while tubing is used for condensers, pipe lines, and other purposes. Much aluminum molding is being employed in the construction of closed-body-type motor cars. Collapsible aluminum tubes are being used in large quantities as containers for non-alkaline toilet articles.

Aluminum wire and cable is a serious competitor for copper in the electrical industry, and aluminum is now used extensively for high-voltage power-transmission lines. Some interesting brochures on the electrical applications of the metal have been issued by the British Aluminium Co., Ltd., and the subject has been discussed in a French report.<sup>67</sup> While aluminum transmission lines have not generally replaced copper, it has been proved that aluminum or aluminum-steel cables are as reliable and efficient as copper cables, and when the price ratio between copper and aluminum is right there is economy in the latter. The principal properties of aluminum and copper from the point of view of their electrical applications are given in Table 11.

The principal uses of aluminum powder and dust are in the aluminothermic (or thermit) process, for the reduction of refractory oxides and the preparation of metals and alloys; in the thermit welding process, for repairing iron and steel castings and for joining rails and other structures; in the calorizing process, for coating metal parts with aluminum; in the manufacture of some explosives; and as aluminum paint. The use of calorized steel pipe in oil-still work has gained ground recently, and the consumption of aluminum powder in calorizing is increasing considerably. Aluminum dust was formerly employed to a slight extent in cyanide practice in place of zinc dust for the precipitation of gold and silver, but this use has disappeared. Aluminum paint has come into wide use in recent years as a non-corrosive, heat-resisting paint, and is being employed on oil tanks, gas holders, balloon- and dirigible-gas bags, and as a general protective paint for both outside and inside (factory) purposes.

The present largest use for light aluminum alloys is for the production of sand castings for automotive work, while die-cast and permanent-mold-cast parts are being used in considerable quantities. Rolled alloys are employed in a minor way, and forgings are just now being developed. The light aluminum alloys have applications in all branches of engineering, including railway work, internal-combustion engines, motor-car manufacture, steam engineering, and marine work, but the automotive industry consumes by far the greatest amount. Other important uses are for aircraft construction, for the manufacture of cast cooking utensils, for vacuum cleaners, for the radio industry, for the electrical industry, for patterns and flasks in founding, for machinery parts, for ornamental wares and for scientific and testing instruments.

The following parts of automobile engines are now regularly produced in light aluminum alloys; crank cases and oil pans, intake and exhaust manifolds, pistons, connecting rods, cylinder-head covers, cylinder water outlet and inlet elbow and tee,

TABLE 11.—COMPARATIVE, MECHANICAL, ELECTRICAL, AND OTHER PROPERTIES OF ALUMINUM AND COPPER<sup>1</sup>

Property	Aluminum	Copper
Specific gravity . . . . .	2 70 ±	8 89 ±
Melting point, degrees Centigrade	658 7	1083
Specific heat (water = 1) at 20°C., caloric	0 214	0 095
Specific thermal conductivity, caloric per degree Centigrade, per square centimeter per centimeter	0 504	0 895
Approximate relative heat conductivity (silver = 100 per cent) . . . . .	50	90
Coefficient of linear expansion, per degree Centigrade	0 000021	0 000017
Tensile strength, hard-drawn wire (No. 10 S.w.g.) pounds per square inch . . . . .	26,000	50,000
Tensile strength, annealed wire (No. 10 S.w.g.), pounds per square inch . . . . .	14,000	29,000
Modulus of elasticity, pounds per square inch . . . . .	10 × 10 <sup>6</sup>	17 5 × 10 <sup>6</sup>
Specific resistance in microhms per cubic centimeter at 20°C.: Annealed . . . . .	2 8159	1 7241
Hard-drawn . . . . .	2 8735	1 7585
Specific resistance in microhms per cubic inch at 20°C.: Annealed . . . . .	1 1086	0 6788
Hard-drawn . . . . .	1 1313	0 6924
Ohms per mil-foot at 20°C.: Annealed . . . . .	16 939	10 371
Hard-drawn . . . . .	17 285	10 578
Resistance of solid conductor, 1,000 yd. long by 1 sq. in. cross-section, ohms: Annealed . . . . .	0 0399	0 0244
Hard-drawn . . . . .	0 0407	0 0249
Coefficient of increase of resistance with temperature, degree Centigrade . . . . .	0 00390	0 00393
Weight per 1,000 yd. by 1-sq. in. cross-section, pounds	3 510	11,520
For hard-drawn conductors of equal resistance: Ratio of diameters . . . . .	1 28	1 0
Ratio of sectional areas . . . . .	1 64	1 0
Ratio of weight . . . . .	0 5	1 0
For hard-drawn conductors of equal temperature rise: Ratio of diameters . . . . .	1 18	1 0
Ratio of sectional areas . . . . .	1 39	1 0
Ratio of weight . . . . .	0 424	1 0

<sup>1</sup> According to the British Aluminium Co., Ltd

cylinder blocks, timing-gear cover, crank-shaft-bearing cups, water pump, and fan and water-pump brackets. Jehle<sup>60</sup> has described an all-aluminum motor car. In passing, it is of interest to call attention to the use of aluminum alloys in the Liberty aviation engine. In the twelve-cylinder model, 225 lb. of aluminum alloys were used, or 27 per cent of the weight of the complete motor. If the aluminum-alloy

parts had been made of cast iron, about 325 lb. would have been added to the motor, making the complete engine weigh about 1,160 lb. The use of aluminum alloys in aircraft engines makes possible weight figures of below 2 lb. per horsepower. The use of aluminum is not confined to the engine in motor-car construction, however. Many other parts are now made in these alloys, so that the car will be as light as possible. In the higher grades of motor cars, aluminum alloys are extensively employed; *viz.*, for cast bodies, transmission cases, differential and worm-gear housings, gear covers, radiator headers and shells, fenders, wheel-hub caps, housings for starting, lighting, and ignition outfits, footboards, steering-wheel spiders, and many miscellaneous small parts.

During the World War period, the development of aircraft was, of course, responsible for a marked increase in the application and uses of light aluminum alloys, and these were employed extensively both in airplanes and dirigibles. The development of the dirigible, and more especially ships of the German Zeppelin, British R-34, and

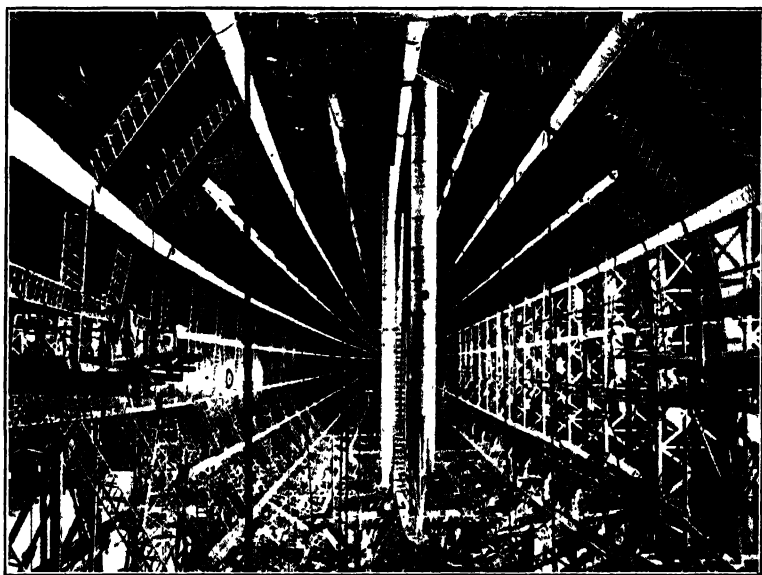


FIG. 13.—Hull structure, British dirigible R-80.

American ZR-1 types, called for a light, strong framework of enormous size, and duralumin and related alloys were found suitable for such frameworks. An idea of the size and complexity of such frameworks may be gained from Fig. 13, showing the hull of the British dirigible R-80, built of duralumin by Vickers, Ltd. Rapid strides have been made in the construction of all-metal airplanes, *i.e.*, heavier-than-air machines, and these are built principally of duralumin. The indispensability of aluminum and aluminum alloys in aircraft construction has been demonstrated beyond any doubt, and in 1918 the Allied governments put 90,000 metric tons of the metal and its alloys into aircraft.

As indicated, light aluminum alloys are used for a great variety of purposes outside the automotive and aircraft fields, and a most recent and interesting development is their widespread use for castings in the electrical manufacturing industry. In this industry, aluminum alloys have replaced cast iron, brass, and bronze for many



parts, *e.g.*, end shields for turboalternators, controller frames, brush holders for synchronous converters, oil circuit-breaker supports, circuit-breaker cross-heads, disconnecting switch bases, switch boxes, clamps, and many small castings. Turbo-alternator end shields weighing as much as 1100 lb. have been poured in a 95:5 Al: Si alloy. The manufacture of electric vacuum cleaners on a large scale is a recent achievement, and aluminum alloys are used extensively in these machines. Some cooking utensils are sand cast in aluminum alloys, and distributors, vats, and other vessels for use in the food-preserving and canning industries are cast in these alloys. Aluminum-alloy castings are used extensively in the manufacture of radio receiving sets, and the development of radio broadcasting has opened up a new field for the application of the metal and its alloys. An increased use for the alloys has followed as a result of the recent international agreement as to limitation of tonnage of battle-ships and auxiliary craft, and aluminum and aluminum alloys are being adopted for a large number of new applications in marine work on the principle that a small saving in weight in many small parts will amount, in the aggregate, to a very material increase in capacity for additional armament or engine horsepower. The more recent and new applications of aluminum alloys are discussed in an article by the writer.<sup>141</sup>

**Melting Practice.**—Aluminum and aluminum alloys are melted in various types of furnaces in practice, and there is really no standardized mode. In foundry



FIG. 14.—Stationary iron-pot furnaces in a foundry.

practice, light aluminum alloys have been melted in all types of furnaces that have been used for brass and bronze, and the iron-pot furnace, so widely used for melting so-called white metals, is the only one employed for aluminum alloys that is not used for brass and bronze. While a great variety of furnaces are in commercial use, as indicated, the iron-pot furnace is generally preferred for melting alu-

minum alloys in foundry practice and the reverberatory-type furnace for aluminum in rolling-mill practice. The theoretical and practical aspects of aluminum and aluminum-alloy melting have been discussed at length by the writer in published papers,<sup>69,70,77,81</sup> which may be consulted for detailed information.

One of the principal difficulties in aluminum and aluminum-alloy melting is the prevention of oxidation (dross) losses, and even with the best practice there is always considerable loss. In practice, the metal and its alloys should be heated only to the required pouring temperature or a little higher, and "soaking" of melts should be avoided. The pouring temperature for aluminum in casting rolling ingots is preferably 700 to 750°C., while in sand practice for 92:8 aluminum-copper alloy, the pouring temperature may vary between 700 and 800°C., depending upon the type of casting. Fuel losses in melting aluminum and its alloys are large, owing to poor furnace efficiency, and the amount of fuel required in melting is about twice that needed for copper and its alloys. The amount of heat required to melt and superheat 92:8 aluminum-copper alloy or aluminum may be taken as 284 cal. per gram = 517 B.t.u. per pound, and if all the calories available in the fuel were utilized, *i.e.*, if the furnace operated at 100 per cent efficiency, it would require the following amounts of different fuels to melt and superheat 100 lb. of aluminum: 4.3 lb. of bituminous coal; 3.7 lb. of anthracite coal; 4.0 lb. of metallurgical coke; 57 cu. ft. of natural gas; 86 cu. ft. of illuminating (city) gas; 431 cu. ft. of producer gas; or 2.7 lb. of fuel oil. In practice, the actual limits as to fuel consumption are 50 to 200 lb. of coal or coke; 0.60 to 15 gal. of fuel oil; and 150 to 1,000 cu. ft. of natural or artificial gas.

**Types of Furnaces and Operation.**—In foundry practice, the following types of furnaces are employed in the United States: coal-, oil-, and gas-fired reverberatory furnaces; oil- and gas-fired stationary and tilting iron-pot furnaces; coal- and coke-fired stationary and tilting crucible furnaces; oil- and gas-fired open-flame tilting, rotating, and stationary furnaces; and electric furnaces of several types. In general, ordinary brass-melting furnaces of various types have simply been adapted for aluminum-alloy melting, while in aluminum rolling-mill work reverberatory and open-flame barrel-shaped furnaces have been largely employed. As indicated, the iron-pot furnace is preferred for melting aluminum alloys in founding, but open-flame furnaces are being used more widely than a few years ago.

In small foundries, and in plants where only a minor part of the output is in aluminum alloys, pit or crucible furnaces are employed largely. The electric-furnace melting of aluminum and its light alloys is receiving considerable attention, and a few installations have been made. The tendency toward the employment of furnaces of large capacity, *i.e.*, reverberatory and open-flame barrel furnaces, has been quite marked lately, and this has necessarily come through the enlargement of plant capacity. On the basis of tests made by the writer, it is recommended that the stationary or tilting iron-pot furnace be employed in small plants and the reverberatory type in large foundries, and in large plants it is good practice to supplement a large reverberatory furnace with the installation of a few iron-pot furnaces. Figure 14 shows an installation of stationary iron-pot furnaces in a foundry.

Turning for a moment to the question of oxidation losses on melting aluminum and its light alloys—when heated in air, aluminum oxidizes to aluminum oxide ( $Al_2O_3$ ), and the rate of oxidation increases rapidly with increasing temperatures. Hence, one of the cardinal rules in melting practice is that the melting temperature should be kept low, and, moreover, heats should not be allowed to soak in the furnace. The

oxidation product resulting on melting is known as "dross," and this ordinarily contains some mechanically entangled metal, the percentage depending upon the care used in skimming the melts. In addition to the temperature, the constitution of the furnace atmosphere in which the metal is melted is of great importance, because of interactions that take place. Thus, in addition to interacting with oxygen, aluminum interacts with nitrogen at normal melting temperature, forming aluminum nitride, and this appears in the dross. Hence, when a furnace is operated with great excess air supply, the dross loss is necessarily high. In speaking of furnace atmospheres, it is quite usual to refer to them as "oxidizing," "neutral," or "reducing," and in melting aluminum and its alloys most melters try to maintain a reducing atmosphere and prevent an oxidizing one in the furnace. From the metallurgical point of view, the terms mentioned have no significance at all unless defined on the basis of (1) the chemical composition of the atmosphere, (2) the kind of metal or alloy melted, and (3) the interactions that take place between the constituents of the atmosphere and the metal or alloy at various temperatures. Aluminum and aluminum-alloy melting-furnace atmospheres have been analyzed by the writer and J. H. Capps,<sup>69</sup> and the conclusion is that, preferably, melting furnaces should be run with practically "neutral" atmospheres, so that the dross loss is reduced to a minimum and the fuel burned efficiently.

**Alloying Practice.**—Prior to the production of any kind of aluminum-alloy manufactures, it is first necessary to prepare the required alloys, and, in practice, the alloys may be prepared and used immediately or they may be prepared and cast into pig form for subsequent remelting. As indicated, the greater part of the aluminum alloys used in the United States is made up in foundries for the production of sand castings, and, as a rule, founders prefer to make up the alloys as required rather than to purchase prepared alloys. Primary aluminum alloys of definite compositions, *e.g.*, 92:8 aluminum-copper alloy, are sold in ingot form for casting purposes and a substantial tonnage of secondary aluminum-alloy pig is made and sold. Primary aluminum alloys, whether pigged or used directly for casting, are made up by adding the alloying metal or metals to aluminum in a melting operation, while secondary aluminum alloys are made by running down scrap aluminum and aluminum alloys, *e.g.*, borings from automotive castings.

Foundry practice in making up alloys for casting varies considerably, and melting charges may consist of the following; (1) all-primary aluminum pig plus the necessary alloying metal, or intermediate alloy required for introducing the additive metal, plus foundry scrap or not; (2) primary aluminum-alloy pig plus foundry scrap; (3) primary aluminum, intermediate aluminum alloy, foundry scrap, and secondary metal; (4) all-secondary metal plus foundry scrap. Other combinations have been employed, and these will readily suggest themselves. In making aluminum-copper alloys, it is usual to make a fixed addition of copper to the aluminum by the use of the intermediate copper-aluminum alloy of nominal composition 50:50 copper-aluminum, known in foundry practice as "hardener." Pure copper and 33:67 and 60:40 copper-aluminum alloys are also employed. The preparation of aluminum-copper alloys has been discussed in detail by the writer.<sup>81</sup>

Iron may be introduced into aluminum alloys by the use of light scrap tin plate or ferroaluminum, while magnesium is best added in small pieces as pure magnesium, using a perforated crucible or "phosphorizer" for containing the metal. Manganese additions are usually made with 25:75 manganese-aluminum alloy, and nickel as light sheet nickel or 20:80 nickel-aluminum alloy. Silicon is added preferably by

using the 50:50 silicon-aluminum alloy. Zinc, tin, and other low-melting-point metals are added as such. An intermediate alloy is essential when high-melting-point metals are to be alloyed, and the employment of these intermediate alloys is a great convenience. Most of them are brittle and can be weighed with accuracy, and their melting points are low, so that the additive metal can be introduced readily without long or high heating. Zinc chloride in small amount is used extensively in melting and alloying practice for aluminum and its light alloys, with the object of cleaning and fluxing the melts. It is efficacious for the purpose. The use of fluxes in melting practice has been discussed at length in the literature, and a paper by Rosenhain and Archbutt may be cited.<sup>105</sup>

**Secondary Aluminum and Aluminum Alloys.**—Secondary aluminum is produced by remelting aluminum scraps and is used largely for remelting in foundry practice for making alloys, although some secondary metal is employed for the production of aluminum rolling ingots. Secondary aluminum alloys are made by remelting aluminum and aluminum-alloy scraps, and such alloys are used largely in foundry practice. In the remelting of aluminum-bearing scraps no refining can be done, as in the case of copper, and, consequently, secondary aluminum and aluminum alloys are normally less pure than the corresponding primary materials. The usual impurities found in secondary aluminum include copper, iron, silicon, manganese, and zinc, while secondary aluminum-alloy pig, say No. 12 alloy, may contain iron, silicon, manganese, magnesium, tin, and zinc, in addition to copper. Practice employed for the recovery of aluminum-bearing scraps is very variable—many types of furnaces are employed, and different fluxes are used. The principal reported investigation on the subject is that by Gillett and James.<sup>39</sup>

While all sorts of aluminum scraps are utilized in making the secondary metals and alloys—including aluminum dross and skimmings, aluminum rolling-mill scrap, aluminum fabricating scrap, particularly from utensil plants, and the corresponding aluminum-alloy scraps—the bulk of the secondary aluminum-alloy pig is produced by smelting aluminum-alloy borings (*i.e.*, chips, drillings, etc.) from automotive castings. Considerable heavy aluminum-alloy scrap results from the junking of old motor cars, and this makes good material for remelting. In machining automotive castings, about 15 per cent of the weight of the castings is removed. Considerable amounts of aluminum dross and aluminum-alloy dross are smelted in secondary practice. In drosses, the content of metallics may run 5 to 60 per cent, depending upon conditions, and the recovery on smelting varies from 40 to 75 per cent. The recovery on smelting borings may be from 40 to 90 per cent of the metal charged, and 80 per cent is good recovery on dirty borings. Recovery naturally depends upon the quality and size of borings, *i.e.*, as to whether the chips are oily, dirty, or clean, and whether large or small. The kinds and characteristics of the aluminiferous scraps available to the secondary smelter have been discussed by the writer.<sup>134</sup> In secondary practice, the determination of the constitution of miscellaneous lots of scraps and their evaluation are important, but the lack of space prevents discussing these items here.

The question of fluxes to be used in secondary aluminum work is of great importance, and a very great number have been suggested, although only a few have been extensively employed in practice. The object in using a flux is to reduce oxidation loss on melting and to cause coalescence of the metal, particularly when melting fine scraps, like borings, and drosses. In practice, the 85:15 sodium chloride-calcium fluoride flux is used most generally, but zinc chloride, several special mixtures of alkali fluorides, and cryolite are also employed. As indicated, the methods of smelting are varied,

and all sorts of methods have been suggested. Heavy scrap can be readily melted with little loss, but special methods are necessary in smelting drosses, borings, and fine scraps. In running borings and drosses, the materials are often charged to a liquid heel in a crucible furnace with a flux, and the mass puddled to insure coalescence of the melted globules, while recently the practice of puddling and working such materials in large reverberatory-type furnaces has gained ground. Drosses are normally crushed and screened to remove aluminum oxide before smelting, while borings are run over a magnetic separator to remove included iron chips. Light scrap, like that from utensil fabrication, may be economically baled before smelting.

The composition of secondary aluminum and aluminum alloys is very variable, but, roughly, the following grades of materials are made: *viz.*, 98 to 99 per cent aluminum pig, No. 12-alloy pig, No. 31-alloy pig, and so-called "casting aluminum." The last mentioned is often poor in quality, since it normally contains excessive amounts of various impurities and is unsuitable for founding. A typical analysis of secondary 98 to 99 per cent aluminum pig is: Cu, 0.42; Fe, 0.82; Si, 0.30; Zn, 0.74; and Al (by difference), 97.72 per cent. A typical analysis of secondary No. 12-alloy pig is: Cu, 7.5; Fe, 1.3; Si, 0.3; Zn, 1.0; and Al (by difference), 89.9 per cent.

**Aluminum-alloy Foundry Practice.**—The aluminum-alloy casting industry is only about twenty-five years old, and its greatest growth has come in the past fifteen years. There are now 2,500 foundries and foundry departments of manufacturing plants in the United States in which aluminum-alloy sand castings are made, and the number is increasing rapidly. As pointed out, about 50 per cent of the world's production of aluminum goes into the manufacture of light alloy castings, and, on the basis of the present output of aluminum, probably about 200,000,000 lb. of castings are now made annually. In trade parlance, aluminum-alloy castings are usually referred to as "aluminum" castings, but it is as incorrect so to speak of these castings as it would be to call brass or bronze castings by the term "copper" castings. Aluminum-alloy foundry practice has been most highly developed in the automotive and exclusive aluminum-alloy foundries, and some of the exclusive aluminum-alloy foundries are large, with outputs of from 2,000,000 to 20,000,000 lb. of finished castings per annum. In the United States, the bulk of the output comes from the Detroit and Cleveland districts.

Any size casting can be made in aluminum alloys, and in practice pieces weighing up to 2,000 lb. have been poured. A casting weighing 500 lb. is considered large, and in ordinary production parts from 1 to 200 lb. are generally made. Very small pieces weighing 1 oz. are cast in sand, but small parts, especially when required in large numbers, are better made by die casting. The minimum thickness of section for sand castings is about  $\frac{1}{8}$  in., and for machining about  $\frac{1}{16}$  in. should be allowed for finish on large castings and  $\frac{1}{16}$  in. for small parts. The size tolerance for ordinary commercial castings is usually given as  $\frac{1}{32}$  in. and the weight tolerance as 3 to 5 per cent. From the point of view of founding, it is of great importance to select alloys which possess good casting properties, and the theoretical aspects of this subject have been discussed in some detail by the writer.<sup>106</sup> Here it is possible only to point out that the production of satisfactory castings with a minimum of wasters depends upon the thorough recognition of the following properties of aluminum alloys: (1) the high contraction in volume, (2) the pasty stage that exists near the melting point and which persists for a relatively long time, and (3) the low strength at elevated temperatures. In general, the most suitable alloy for casting is the one having the least contraction on freezing.

**Molding Sands and Core Sands.**—The ordinary molding sands that are used for brass are suitable for aluminum alloys, and in the United States the well-known Albany sands are employed considerably. Certain Ohio, Kentucky, Michigan, Illinois, and New Jersey sands are also used. Thames sand has been imported from England for aluminum-alloy work, although quite needlessly, since it is very similar in texture, analysis, and behavior in the foundry to Albany sand. Similarly, sands have been imported from France, with the mistaken idea that foreign sands possess some undescribed properties which make them especially suitable for light-alloy founding. There are ample sources of sands for both molding and core work in the United States. A typical Albany sand has the following analysis: loss on ignition, 1.95;  $\text{SiO}_2$ , 80.52;  $\text{Fe}_2\text{O}_3$ , 4.83;  $\text{Al}_2\text{O}_3$ , 8.39;  $\text{CaO}$ , 0.67;  $\text{MgO}$ , 0.64;  $\text{Na}_2\text{O}$ , 1.25; and  $\text{K}_2\text{O}$ , 1.45 per cent. The rational analysis is; clay substance, 19.85; quartz, 50.50; and feldspar, 29.65 per cent. In molding aluminum-alloy castings, the sand should be worked rather dry, and the molds rammed rather lightly. The water content of tempered sand is 5 to 10 per cent, and 7 per cent water added to dry sand is suitable for average work. Burning-on difficulties which occur in steel-castings production are not met with in aluminum-alloy founding, but the increased tendency to oxidation and the greater mobility and sand-searching power of aluminum alloys present peculiar difficulties.

A large variety of core-sands and mixtures of sands, as well as binders, are employed in aluminum-alloy founding. Cores should be made so that they will crush readily and offer no resistance to the normal shrinkage of the casting. A hard core will cause strains to be set up, so that the metal will fracture. Hence, the cores should be light and soft. Some special core sands, such as Providence river sand, are handled by dealers especially for aluminum-alloy castings, but usually particular mixtures are employed. Thus, a mixture used by one foundry consists of 3 parts new core sand (sharp white sand), 1 part new molding sand, and 4 parts old burnt core sand; this is mixed in the ratio 1:20 or 1:25 binder:sand. Dextrin, oil, resin, and other commercial binders are employed in core-sand mixes. The tendency in aluminum-alloy foundry practice is toward the use of green-sand cores wherever possible, because of the greatly decreased production costs which may be effected by their employment, rather than dry-sand cores. Green-sand cores are used largely in the founding of large automotive castings, as body cores for crank cases, oil pans, and transmission housings. Dry-sand cores are used practically exclusively for some kinds of automotive castings, such as manifolds and carburetors.

**Practical Aspects of Founding.**—While the details of foundry practice cannot be discussed here, a few general principles may be laid down to ensure the production of good castings. The melting stock should be carefully selected and mixed so as to give the required alloy, and heats should be under strict chemical control. The alloy should be melted in a non-oxidizing or neutral atmosphere, care being taken that no part of the charge be overheated. Molds should be prepared waiting to be poured, rather than to have the alloy standing in the furnace waiting for molds. The alloy should be cast at the correct pouring temperature. The mold into which the alloy is poured should be carefully prepared, and one of the most important considerations is that of cleanliness. Among other factors, the following are of the utmost importance as regards the preparation of molds: (1) the gates should be properly proportioned, correctly distributed, and

placed in the right positions; (2) the gates should be designed so as to choke and skim the alloy before it enters the mold cavity; and (3) there should be a sufficient number of risers, properly placed, of the correct size to feed all sections.

Blowholes, porosity, unsoundness, and other defects in aluminum-alloy castings and poor mechanical properties occur together, and the general principles of founding, applied to produce good mechanical properties, will tend to eliminate wasters to a great extent. As has been pointed out, the pouring temperature of light aluminum alloys has a great effect upon the strength, soundness, and general properties of the alloy, and the general rule in foundry practice is that all castings should be poured at as low a temperature as is possible and still have the alloy fill the molds and also avoid cold shuts. The pyrometric control of melting and pouring temperatures is essential to the production of good castings. The pyrod is a good type of pyrometer.

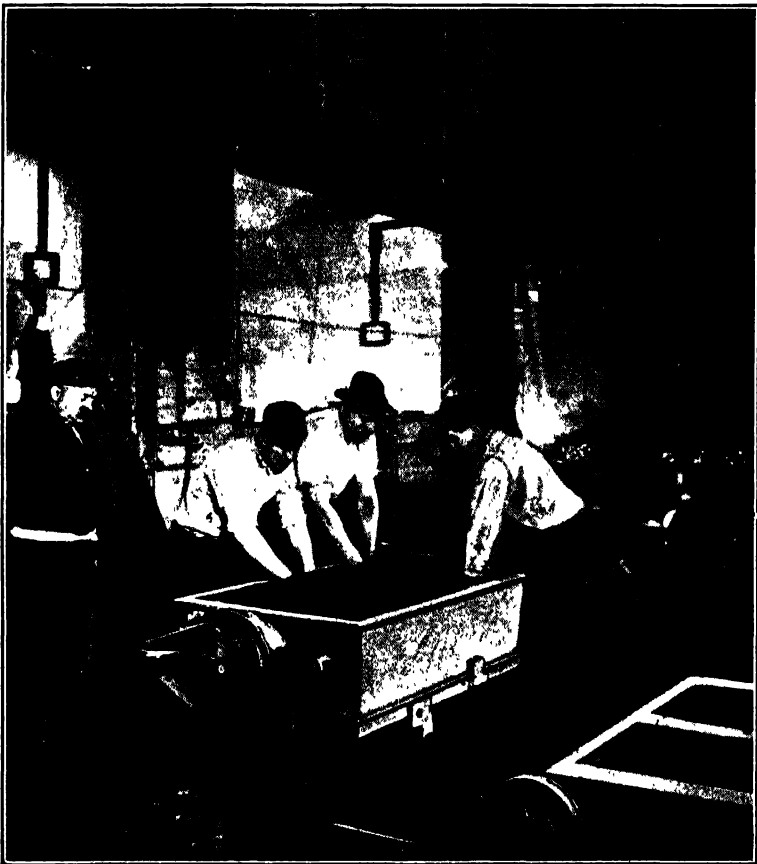


FIG. 15.—Crank-case molding in a roll-over machine. (Osborn Mfg. Co.)

**Molding Methods.**—The first item for consideration in the production of castings is the design of the parts and the preparation of the patterns. Pattern makers usually allow a shrinkage of 0.156 in. per foot, but this is unsafe, and the actual contraction of the different alloys used should be determined.<sup>108</sup> Castings

should be designed so that the variations in thickness of contiguous sections are as small as possible, and sharp changes in direction, are to be avoided as are thin sections and complicated coring. Where thin and thick sections are in contiguity, ample connecting fillets should be used. The required porosity in the sand can be obtained by using properly selected and tempered sands and by light and even ramming. Hard ramming should be avoided. In gating, large and complicated castings are best run from bottom gates, since these give more even flow of metal and prevent displacement of cores. Large gates and risers are recommended, so that the metal will not be restricted in its flow in the mold and all sections will be adequately fed. Risers should be attached to those parts of the casting that solidify last. Chills are used frequently, particularly where large masses of metal are contiguous to light, thin sections, and they are useful in preventing cracks.

Machine molding is used extensively for large castings, and Fig. 16 shows a step in the process of molding a crank case on a jar-rammed rollover molding machine. The sand is being tucked in around the pattern. After a rough casting has been shaken out of the mold, the core sand is removed, the gates and runners knocked off by hammers or cut with a band saw, and all fins, gate lugs, and other small protuberances are removed by chipping and grinding. After rough cleaning, the castings may be sand blasted, and then are sent to the machine shop.

**Defects in Castings.**—Casting losses in the production of aluminum-alloy sand castings are normally rather high, and the average loss due to wasters in founding automotive castings is 10 to 15 per cent. About 75 per cent of the wasters are caused by molding technique, and the remainder by metallurgy, melting, and miscellaneous causes. Rejections vary considerably in different foundries, depending upon the type of casting made and local conditions. Furthermore, different castings are rejected for different reasons. Porosity and leaks cannot be tolerated in crank cases, manifolds, and carburetors, but these same defects are not serious in clutch cones, and some kinds of housings and carriers. On the other hand, surface sand holes are sufficient cause for rejection in many kinds of castings which must be highly polished, such as vacuum-cleaner housings and parts, wheel-hub caps, and instrument frames.

In practice, castings may be rejected for defects resulting from one or a combination of causes, including cracks, sand holes, chill blows and core blows, cold shuts, hard inclusions ("hard spots"), porosity and general unsoundness, blowholes, run-outs and misruns, uneven walls and cut-throughs, breaks in trucking, handling, chipping, cleaning, and welding, draws, and such defects as are traceable to hard ramming and soft ramming, dirty and broken cores, sand or paste in the cores, crushed molds, washed-in gates, poor patching, wet sand, broken molds, cope drop, and other items. The regulation of shrinkage and the prevention of cracks are two of the more serious difficulties in the production of aluminum-alloy castings, and rejections because of shrinkage and cracks are heavy on the average. In general, many of the present casting losses in founding could be prevented by adequate inspection of molds before closing, and many of the defective castings made can be salvaged by welding and other repairs. Casting losses and methods for the prevention of wasters have been discussed at length by the writer in published papers.<sup>62, 71</sup>

**Some Typical Defects.**—Of the various defects that may occur in sand castings of aluminum alloys, the three most frequent and important are: (1) blowholes,



porosity, and general unsoundness; (2) hard inclusions; and (3) cracks. Blow-holes are caused primarily by too high melting and pouring temperatures, and can be largely prevented, but general unsoundness is more difficult to overcome. As a rule, aluminum-alloy sand castings tend to be unsound, and in practice it is necessary to make tests on inspection, in certain types of castings, for porosity and related defects.

The usual method employed for detecting general or local porosity in such castings as crank cases, oil pans, manifolds, etc. is the open test with a solution of methylene blue in gasoline. In the test, this liquid is painted or smeared on the casting, and if the part is porous, the solution will seep through and show on the other side. Air-pressure, water-pressure, and steam-pressure tests are also applied, particularly to hollow castings, for detecting porosity and leaks. Porous castings may be treated, *i.e.*, the porosity closed, by several methods, of which the sodium silicate method is the one most commonly employed. In this, the castings are first soaked in concentrated (40°Bé., 1.38 sp. gr.) sodium silicate solution for an hour, then immersed for 1 to 2 min. in dilute sulphuric acid (25 per cent), and then washed in water. The casting is then dried at above 100°C. for at least 1 hr. Porous castings may also be treated with bakelite. The general subject of blowholes, porosity, and related defects in aluminum-alloy castings has been discussed at length by the writer.<sup>51</sup>

The occurrence of hard inclusions, *i.e.*, the so-called "hard spots" of foundry parlance, in aluminum-alloy castings is of interest and importance to founders and users of parts. In some cases, the percentage of machine-shop returns, owing to rejections because of hard inclusions, may be high and be the cause of considerable loss. Hard inclusions differ so widely in character that the term "hard spots" is only roughly descriptive, but "hard spots" are ordinarily defined as any kind of metallic or non-metallic inclusions that cause difficulty on machining or polishing. When a machine tool strikes a hard inclusion, its edges are quickly dulled and rendered unfit for cutting. All hard inclusions may be divided into two classes, *viz.*, (1) non-metallic inclusions, and (2) metallic inclusions. Under the former are included all hard, foreign, non-metallic particles, such as pieces of brick or cement, chunks of crucibles, core sand and molding sand, and hard clay, that may be charged with the melting stock. Metallic hard inclusions are generally traceable to iron, and are due to actual iron or steel, such as nails, core wire, chaplets, chills, etc., charged into the furnace, or to the hard intermetallic compound  $\text{FeAl}_3$  caused by the dissolution of iron or high iron in the melt. The subject of hard inclusions in aluminum-alloy castings has been discussed at length by the writer.<sup>50</sup> They can be practically entirely prevented by clean melting practice.

Cracks in aluminum-alloy castings constitute the most serious defect encountered in founding, and if the average casting loss be taken as 10 per cent, the wasters because of cracks amount to 2 per cent of the castings poured, or 20 per cent of the total defectives. The usual commercial aluminum alloys are subject to cracking when poured into molds, owing to their large contraction in volume on freezing and their hot shortness, and, so long as complicated castings are made, cracks must be expected in production. Some of the principal factors affecting the occurrence of cracks are: the composition of the alloy; the method of molding; and the design of the castings, particularly as to thick and thin sections in contiguity. In general, the less the contraction in volume of the alloys the less the cracking. The silicon-bearing aluminum alloys are particularly good for casting, since they have little tendency to crack—their contraction in volume is relatively low as compared with the other alloys. The causes of and methods for the prevention of cracks have been discussed by the writer in another place,<sup>97</sup> where detailed information will be found.

**Die Casting and Permanent-mold Casting.**—Aluminum-alloy castings are made by two other processes than sand casting; *viz.*, by die casting and permanent-mold casting, but the total production by these methods is subordinate to the output of sand castings. In die casting, special steel dies or molds are employed, while in permanent-mold work cast-iron molds are generally employed. The use of metallic molds for castings production finds justification in the fact that practically all castings made in sand molds require considerable machining, and that, by the use of a metallic mold of some kind, castings which are more accurate as to size and weight tolerances and which require little or no machining can be made. Practically any mechanical part, unless too large, can be made by die casting or permanent-mold casting, and castings made by these processes may be practically finished parts when they come from the mold. A 20-

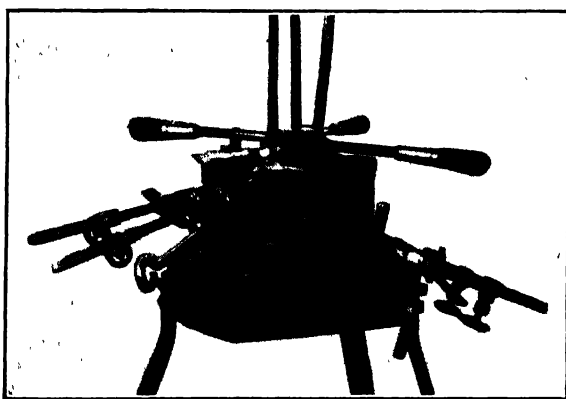


Fig. 16 —Mold for aluminum alloy piston production.

lb. casting is considered large in permanent-mold work, but castings up to 200 lb. have been poured. The minimum weight may be taken as about 1 oz. A 10-lb. casting is considered large in die-casting work, and very small pieces weighing  $\frac{1}{4}$  oz. are made. The minimum section thickness for die castings is about  $\frac{1}{16}$  in. and that for permanent-mold castings is  $\frac{1}{8}$  in. Die castings may require no stock for finishing if tolerances of  $\pm 0.003$  in. are allowed. The same alloys used for sand casting are employed in die casting and permanent-mold work, but some special alloys have been developed for particular use in metallic molds.

A die casting is a finished casting made by forcing a liquid alloy under pressure into a metallic mold or die. Air pressure is used ordinarily for aluminum-alloy die castings. A permanent-mold casting is a product obtained by pouring a liquid alloy into a metallic mold, the metal going into the mold under the force of gravity. Die casting is essentially a quantity production process, and few parts can be considered practical die-casting jobs in less than 1,000 lots, because of the heavy expense involved in making the dies. The cost of any die casting must be less than the combined cost of producing a sand casting plus the cost of machining to a finished product equivalent to a die casting. It should be pointed out that aluminum-alloy die castings made on compressed-air machines are exceptionally unsound and full of blowholes. The outer shell has a good surface appearance, but if that shell is removed by machining, the unsound and blowhole character of the interior will be revealed. Hence, such castings should not be used where strength is essential.

The process of die casting consists essentially in melting the alloy in a suitable container and then forcing it, by suitable means, under pressure into a metallic mold or die. As stated, aluminum-alloy die castings are made largely on compressed-air machines, but in Europe such castings are also made by mechanical pressure, *i.e.*, by the Cothias system. Various compressed-air machines are in use in the United States, among which may be mentioned the Hakanson, Kralund, Bungay, Doehler, Stewart, and Sandage types. Such machines are generally semiautomatic in operation. In casting, the alloy is maintained at 700 to 750°C., and the dies are run at 350 to 500°C., depending upon the type of casting and the rapidity of operation. The air pressure for forcing the alloy into the dies varies from 100 to 1,500 lb. per square inch, and for the ordinary run of castings may be about 500 lb. Each half of the die may be made of a large number of component members, but when assembled the dies must open and close in two sections. The internal cavities, holes and other irregularities on a casting are produced by steel cores. The dies are ordinarily made of chrome-vanadium steel, and the cores may be made of the same steel or of tungsten steel. When properly heat treated, chrome-vanadium steel dies will last for 10,000 to 15,000 or more casts. Tour<sup>96</sup> has discussed the performance of dies. The 92:8 and 90:10 aluminum-copper alloys have been employed generally for die casting, but some special alloys including 90:2:8 aluminum-copper-silicon and 90:8:2 aluminum-copper-nickel alloys have been employed considerably. Aluminum-alloy die castings are adapted to a variety of uses, notably in the form of small parts for automotive construction in the manufacture of automobiles and aircraft, for vacuum cleaners, radio-set parts, household appliances, adding machines and typewriters, and various small parts of light machinery.

It has been stated that the term permanent-mold castings is used to connote the product obtained by pouring liquid alloys into metallic molds, the metal going into the mold under the force of gravity, and yielding a casting. In the literature, permanent-mold castings have often been confused with die castings. The permanent-mold process has been used largely for the production of aluminum-alloy pistons for internal-combustion engines, but numerous other kinds of castings are made commercially. The process is confined largely to the manufacture of castings in which metallic cores can be used, but some castings have been made using sand cores. The essential features of permanent-mold castings are similar to those of otherwise identical die castings, but the former are sound, whereas the latter are not. Moreover, the tensile properties of permanent-mold cast alloys are normally much better than sand-cast ones. The process may be regarded as standing intermediate between sand casting and die casting, and it has a definite field not covered by either. The process consists essentially in assembling the mold, heating it to the proper temperature (in practice the mold is kept hot by burners), inserting the cores, and pouring the alloy. The cores are removed in the proper order and at a suitable interval of time after the alloy has been poured, and the mold is then taken apart so that the casting can be removed. Székely<sup>1</sup> has patented the general principles of permanent-mold casting, but many improvements have been made recently in the construction and operation of molds for the production of particular kinds of castings.

Permanent molds are generally made of gray cast iron, and the cores are made of 3.5 per cent nickel steel or other special alloy steels. Molds made of cast iron high in graphitic carbon and low in combined carbon are preferred, and a typical analysis of such an iron is: combined carbon, 0.14; graphitic carbon, 3.35; Si, 2.40; Mn, 0.43; S, 0.10; and P, 1.3 per cent. Mold temperatures are variable, but for piston production molds are operated at 325 to 525°C., and the cores are kept somewhat cooler. Washes and coatings for the inside surfaces of molds are practically useless and need not be applied. However, a mixture of sodium silicate and lime made into a thin paint with

<sup>1</sup> U. S. Patent 841279, Jan. 15, 1907.

water is frequently employed. The production of aluminum-alloy pistons in permanent molds has been discussed by the writer and M. E. Boyd.<sup>107</sup> Figure 16 shows a view of a permanent mold for pouring aluminum-alloy pistons. In addition to being used for pistons, permanent-mold casting has been extended to the production of many parts ordinarily made by sand casting or die casting. The process gained much ground in the period 1922 to 1925, and is now a serious competitor of both sand casting and die casting.

**Mechanical Treatment of Aluminum and Aluminum Alloys.**—As indicated previously, about 50 per cent of the aluminum production is used for making light alloy castings, while the remainder is used as substantially pure aluminum, largely in fabricated form. The production of worked manufactures in aluminum alloys is just now being developed, and the total output of worked aluminum alloys (rolled, drawn, forged, and extruded parts) is relatively small as compared with the output of cast alloys. Substantially pure aluminum is rolled into sheets of various gages, from Nos. 10 to 40 American wire gage (B. & S. gage), to be used for fabricating; drawn into wire for electrical conductors; and drawn or extruded into bars, rods, tubes, molding, channels, and special shapes. Very thin aluminum foil is made, as well as powder, dust, and granulated aluminum. Some aluminum-alloy sheet is rolled, largely in 98.5:1.5 aluminum-manganese alloy and in duralumin, but very little aluminum-alloy wire is produced. Aluminum-alloy forgings, largely in duralumin, are being made commercially at the present time, and the use of such forgings is expected to increase. The specific tenacity of certain forged aluminum alloys equals that of forged 3 per cent nickel steel. Rolled, drawn, and extruded aluminum alloys have been used for a number of years, but not in important amount; however, the employment of extruded sections in aircraft has been general, and the production of sections by extruding is a desirable method of manufacture.

**Rolling Practice.**—The details of rolling-mill practice for aluminum have been treated in detail by the present writer and M. B. Anderson.<sup>59</sup> The sequence of operations in the production of aluminum or aluminum-alloy sheet is about as follows: (1) melting of the aluminum (and, in alloys, preparation and melting of the alloy); (2) pouring the ingots; (3) preheating the ingots to the proper temperature for breaking down into slabs; (4) breaking the ingots down hot into slabs; (5) slabbing, *i.e.*, further reduction either hot or cold; (6) roughing; (7) finishing; (8) annealing and heat treatment when required.

Aluminum and aluminum-alloy sheet rolling differs from steel, brass, and copper rolling in the relatively low temperatures employed for hot work, and, further, finishing to final gage is usually performed in the cold.

In casting rolling ingots, the metal or alloys are poured into vertical, tilting, book-type, cast-iron molds or into horizontal open molds; the former are preferable. Coatings are unnecessary for the inside surfaces of the molds. The pouring temperature for casting aluminum rolling ingots is 700 to 750°C., and the light aluminum alloys are usually poured slightly lower. Ingots are cast in various sizes, depending upon the size sheet to be rolled. A common size used in American practice for wide sheets is 4 by 12 by 17 ins., weighing about 75 lb., while for rolling strip, coils, and narrow sheets, smaller ingots, *e.g.*, 3 by 12 by 32 in., 2 by 12 by 24 in., and 1½ by 12 by 18 in., are used. After casting, the ingots are heated in ingot-heating furnaces to 425 to 450°C. for aluminum and 450 to 480°C. for duralumin, prior to rolling. At some works, aluminum ingots are rolled directly from the molds, but this is bad practice. From the ingot-heating furnace, the ingots are broken down hot in a two-high mill to slabs. Old machine oil or kerosene is sprayed on the rolls to prevent the slabs from sticking. For aluminum in wide sheets, the slabs are then cold slabbed on

a mill to about half their original thickness, then roughed to within about two gage numbers of the finished gage, and finally rolled on finishing mills to the required gage. All rolling from the hot-mill slab may be done entirely without annealing between passes, but for some alloys of the duralumin type it is necessary to anneal fairly frequently in order to reduce cracking. Aluminum is produced as wide sheets and as strip or coil metal. The former are run on wide finishing mills and the latter on mills with narrow rolls, or strip mills. Figure 17 shows an aluminum rolling mill with rolls 16 by 30 in. In making planished sheet, the roll surfaces are kept bright and smooth with buffs, while in making gray plate the sheets are finished on unpolished rolls.

Aluminum sheet is furnished in various hardness, *e.g.*, hard rolled, intermediate, and dead-soft annealed. The hardness is that given by the Shore scleroscope, and

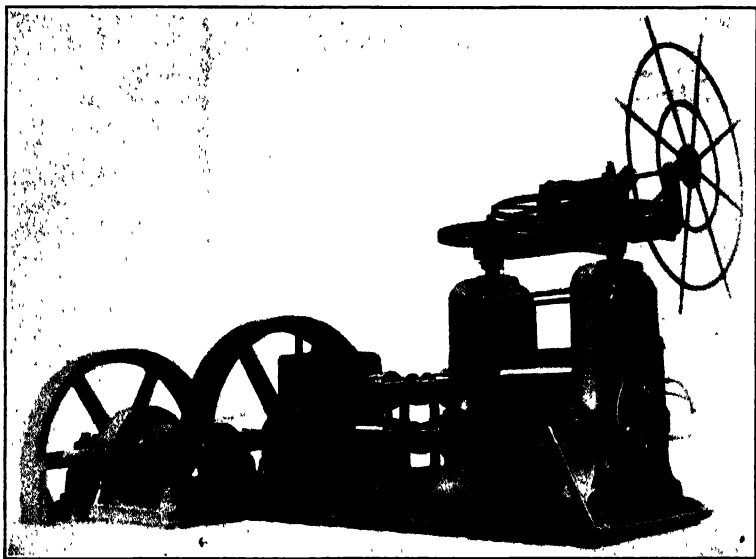


FIG. 17.—Aluminum-sheet finishing mill. (W. H. A. Robertson & Co., Ltd.)

in intermediate sheet varies over a considerable range. The intermediate grades are made by annealing during the course of rolling and before the final passes. Hard-rolled sheet is the product obtained by cold rolling from the slab to finished gage, while dead-soft annealed sheet is made by full anneal on hard-rolled sheet. Annealing is carried out by heating for 2 to 3 hr. at  $400^{\circ}\text{C}$ ., and the metal can be softened by a rapid anneal at moderately high temperature. The annealing of aluminum sheet has been discussed at length by the writer.<sup>43</sup> Table 12 gives the weights of aluminum sheets in various gages and those of slabs in various thickness. Aluminum foil is made by rolling sheet very thin on special foil mills, or else thin sheet may be worked under the hammer until the required thinness is obtained.

**Forging Practice.**—In forging aluminum alloys, the temperature range is restricted for hot working, since the alloys are hot short, and the proper temperatures for different alloys are worked out by trial. In the production of forgings, the sequence of operations may be as follows: (1) preparation and melting of the alloy; (2) pouring the ingots; (3) preheating the ingots to the working temperature; (4) hot working or cogging into a billet, bloom, or slab; (5) hot forging to

TABLE 12.—WEIGHTS OF ALUMINUM SHEETS AND SLABS IN VARIOUS GAGES AND THICKNESSES

Sheet gage, A.w.g.	Thickness, inch	Weight per square foot, pounds	Sheet gage, A.w.g.	Thickness, inch	Weight per square foot, pounds
0000	0.4600	6 406	19	0.0358	0.499
000	0.4096	5 704	20	0.0319	0.445
00	0.3648	5 080	21	0.0284	0.396
0	0.3248	4 524	22	0.0253	0.353
1	0.2893	4 029	23	0.0225	0.314
2	0.2576	3 588	24	0.0201	0.279
3	0.2294	3 195	25	0.0179	0.249
4	0.2043	2 845	26	0.0159	0.221
5	0.1819	2 534	27	0.0141	0.197
6	0.1620	2 256	28	0.0126	0.176
7	0.1442	2 009	29	0.0112	0.156
8	0.1284	1 789	30	0.0100	0.139
9	0.1144	1.594	31	0.0089	0.124
10	0.1018	1 418	32	0.0079	0.110
11	0.0907	1 264	33	0.0070	0.098
12	0.0808	1 126	34	0.0063	0.087
13	0.0719	1 002	35	0.0056	0.078
14	0.0640	0.892	36	0.0050	0.069
15	0.0570	0.796	37	0.0044	0.062
16	0.0508	0.707	38	0.0039	0.055
17	0.0452	0.630	39	0.0035	0.049
18	0.0403	0.561	40	0.0031	0.043

## Slabs

Thickness, inch	Weight per square foot, pounds	Thickness, inch	Weight per square foot, pounds
$\frac{1}{16}$	0.869	$\frac{9}{16}$	7.827
$\frac{1}{8}$	1.739	$\frac{5}{8}$	8.697
$\frac{3}{16}$	2.609	$1\frac{1}{16}$	9.567
$\frac{1}{4}$	3.479	$\frac{3}{4}$	10.435
$\frac{5}{16}$	4.348	$1\frac{3}{16}$	11.306
$\frac{3}{8}$	5.218	$\frac{7}{8}$	12.175
$\frac{7}{16}$	6.088	$1\frac{5}{16}$	13.045
$\frac{1}{2}$	6.958	1	13.914

final shape; and (6) heat treatment if required. Duralumin is the principal alloy used for forging, but the 97:3 aluminum-copper and 97:2:1 aluminum-copper manganese alloy have been employed. While some forgings have been made by

working a cast ingot, ordinary practice calls for a preliminary working by rolling, and the final shaping is done on a piece cut from a rolled billet or slab. Duralumin is forged in the range at 450 to 480°C., and the 97:2:1 aluminum-copper-manganese alloy may be given preliminary forging at 500°C., and then finished at 300°C. Finishing temperatures are varied according to the strength desired, and fairly cold forging may be done as low as 250°C. Duralumin forgings are heat treated after shaping, in order to give the parts the required mechanical properties. Forging is done under the hammer, as in steel forging, but the blows are lighter. Substantially pure aluminum is forged occasionally, *e.g.*, the ends of aluminum conductor rods are forged for making bus-bar connections.

Forged duralumin may have a tensile strength of 55,000 to 62,000 lb. per square inch, a yield point of 30,000 to 36,000 lb., an elongation of 18 to 25 per cent, and Brinell hardness of 93 to 100. These figures refer to heat-treated forgings. Duralumin forgings are now being used as connecting rods on several standard American motor cars. Forged duralumin rims and pressed axle housings have been used in automotive construction.

**Drawing Practice.**—Aluminum is ductile and can be readily drawn into shapes, sections and wire. In late years, the extrusion process has come into general use for the production of sections, bars, and tubes in both aluminum and its light alloys, but wire is made by drawing on a bench. Rods and wire are first hot rolled and then cold drawn to size or gage. The methods used are similar to those for copper. In wire drawing, wire bars or billets are rolled to  $\frac{3}{8}$  to  $\frac{1}{2}$ -in. rounds, and these rods are then cold drawn to final gage. Tallow is employed as the lubricant, and the drawing speeds vary from 150 ft. (initial) to 600 ft. (final) per minute. In drawing tubes, plates are first cupped, as in brass-tube manufacture, and then drawn on a press, followed by drawing on the draw bench. Such drawing may be done cold, but annealing between draws is done if necessary. Aluminum wire is made in various sizes from Nos. 0000 to 35 American wire gage (B. & S. gage). Drawn sections are made in practically any required shape. Aluminum and aluminum-alloy rivets, bolts, nuts, and similar products are made by screw-machine operations on rods.

**Extrusion Practice.**—Aluminum and its light alloys are extruded into various sections. The extrusion process consists in forcing an ingot, previously heated, through an aperture—the extruded metal naturally taking the shape of the aperture through which it is forced. By extrusion, sections can be made in one operation to the required size. Extrusion is an improved method for producing bars, rods, tubes, and sections of any desired shape, and it is expected to supplant drawing for many shapes. Substantially pure aluminum is very suitable for extrusion, owing to its malleability at the working temperature; some aluminum alloys are suitable, but others are not. The temperature in extruding varies among the different alloys, and the pressure employed is a function of the properties of the alloy and the temperature used. Considerable experimental work on extruding aluminum alloys has been carried out by Rosenhain and his co-workers<sup>66</sup>.

In the process, the sequence of operations is as follows: (1) preparing and melting the alloy; (2) pouring the ingots; (3) preheating the ingots to the working temperature; (4) extruding; and (5) heat treatment, if necessary. Short ingots are normally used for extrusion in order to keep the ram pressures on the extrusion presses

as low as possible. An ordinary size of ingot is 5-in. diameter and the length may be up to 24 in. In extruding, the heated ingot is placed in the pressure chamber of the extrusion press, and the ram or plunger is forced against it so that the alloy is made to flow through a hardened die which is held securely in a strong head. The dies may be made with one or a multiplicity of apertures, say up to four, so that with small sections several pieces are made with one stroke of the ram. In extruding tubes and other hollow sections, a hollow ingot is used. The temperature for extrusion is 350 to 500°C., depending upon the alloy and the size and shape of the section.

Aluminum and duralumin are used most frequently for extruding, and experiments have been made with many alloys, particularly 77:3:20 aluminum-copper-zinc and 92.5:4:1.5:2 aluminum-copper-magnesium-nickel. Substantially pure aluminum when extruded may have tensile strength up to 34,000 lb. per square inch and elongation of 5 per cent. With extruded rods of 77:3:20 aluminum-copper-zinc alloy, values up to 60,000 lb. have been obtained for the tensile strength, and up to 20 per cent elongation.

**Metallography.**—The methods of X-ray crystal analysis applied to the structure of metallic aluminum assign a face-centered cubic arrangement to its atoms. The length of the side of the elementary cube is 4.046 Å.U. and the distance of closest approach of the atoms is 2.86 Å.U. Aluminum is not allotropic. A metallography for aluminum and its light alloys comparable to that set up for steel has now been worked out, and the microstructures of alloys in many binary, ternary, and some quaternary aluminum-alloy systems have been studied in connection with investigations of the diagrams of thermal equilibrium. Metallography as a method of test and control of quality has not yet been extensively applied in the production of aluminum and aluminum-alloy manufactures, owing largely to the difficulties experienced in the preparation of microsections. In recent years, considerable work on the constitution of aluminum alloys has been done at the National Physical Laboratory, England, and new diagrams for a number of systems published in the *Journal of the Institute of Metals (q.v.)*. Considerable work has been done by Carpenter and his collaborators<sup>40, 92</sup> recently on the microstructural changes occurring on heating worked aluminum.

In preparing sections of aluminum and its light alloys for microscopic examination, it should be remembered that the materials are soft and easily scratched, and aluminum is one of the most difficult metals to polish. Etching reagents for distinguishing metallographic constituents in aluminum and aluminum alloys are only imperfectly developed. While the general plan of preparing microsections of aluminum and its alloys is similar to that for steel, the ordinary methods used for steel are totally useless for aluminum. Thus, when the metal is ground on fine emery papers it becomes badly darkened, owing to the emery particles working into the mass. This is overcome by smearing the papers with paraffin. Methods for preparing sections have been described by Hanson and Archbutt,<sup>50</sup> by the writer,<sup>42, 47, 49</sup> by Dix,<sup>82, 98</sup> and others. The method of Dix may be described briefly. The section to be prepared is first ground on a coarse wheel, and then on a finer wheel to secure a plane surface for subsequent operations. The section is next ground by hand on emery papers of succeeding fineness (*e.g.*, French Hubert of four succeeding grades), and the two finest papers are covered with paraffin dissolved in kerosene in order to prevent the emery particles from becoming embedded in the specimen. The next operation, after washing, consists in running on a broadcloth disc using Norton 65F alundum as the abrasive. Final polishing is done on a broadcloth disc using heavy magnesia powder as the polishing agent. Excellent structures in aluminum and its alloys can be



developed by relief polishing. Figure 18 shows the microstructure of impure aluminum pig.

The presence of hard constituents, such as  $\text{FeAl}_3$ ,  $\text{CuAl}_2$ ,  $\text{NiAl}_3$ , etc., in aluminum alloys can be readily detected by relief polishing of sections, but etching is ordinarily necessary to reveal the internal structure. Various etching reagents are employed for distinguishing different constituents. Dilute sodium hydroxide in aqueous solu-



FIG. 18.—Dark silicon and half tone constituent X in impure aluminum pig; unetched;  $\times 1000$ . (Dix.)

tions (0.1 to 10 per cent) is used considerably as is dilute hydrofluoric acid for developing structure. When etched with either of these reagents, the section is darkened, and the dark smudge is removed by dipping momentarily in concentrated chromic or nitric acid. An immersion of  $\frac{1}{2}$  to 1 min. in 10 per cent hydrofluoric acid is suitable for aluminum sheet. Figure 19 shows the microstructure of hard-rolled aluminum

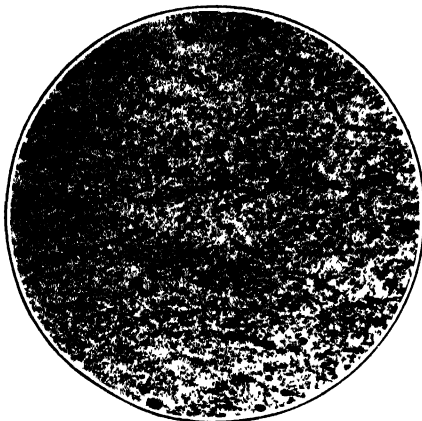


FIG. 19.—Hard rolled aluminum sheet; etched HF;  $\times 100$ .

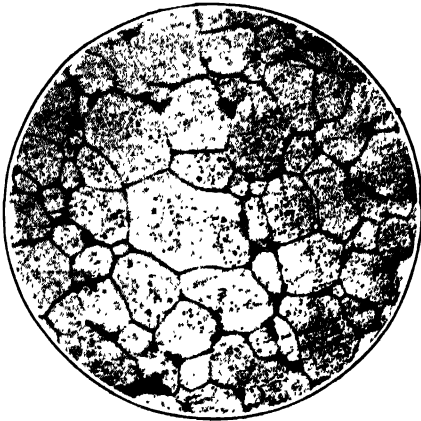


FIG. 20.—Aluminum sheet after annealing; etched HF;  $\times 50$ .

sheet, and Fig. 20 shows the same sheet after annealing. The usual impurities in aluminum are copper, iron, and silicon. In the amounts present, copper is in solid solution, iron forms the intermetallic compound  $\text{FeAl}_3$ , and silicon may occur as free silicon and as the constituent X ( $\text{AlFeSi?}$ ). In aluminum alloys, copper forms the intermetallic compound  $\text{CuAl}_2$ , which is soluble in aluminum in the amount of 5 per cent at  $540^\circ\text{C}$ . and 3 per cent at  $20^\circ\text{C}$ . The binary 92:8 aluminum-copper alloy con-

sists of the aluminum-CuAl<sub>2</sub> solid solution plus the CuAl<sub>2</sub> eutectic. Iron forms the compound FeAl<sub>3</sub>, which is apparently insoluble in aluminum in amounts over 0.15 per cent. Magnesium forms the compounds Mg<sub>2</sub>Al<sub>3</sub> and Mg<sub>3</sub>Al<sub>2</sub>; magnesium is soluble in aluminum up to 11 per cent at 420°C. and 9.5 per cent at 150°C. With silicon, magnesium forms the compound Mg<sub>2</sub>Si, which is found in duralumin. Manganese and nickel form the compounds MnAl<sub>3</sub> and NiAl<sub>3</sub>, which are but slightly soluble in aluminum. Zinc is soluble in aluminum in the amount of 18 per cent at 20°C. and 35 per cent at 250°C. Most of the metallographic constituents can be identified by suitable etching reagents.<sup>60</sup>

**Heat Treatment.**—Both wrought and cast aluminum alloys are heat treated commercially, and a wide field has thus been opened. Worked aluminum is annealed, as are the alloys, for the purpose of softening, and some cast alloys are annealed to release casting strains. Aluminum-alloy pistons are annealed to overcome growth and distortion. That alloys of the duralumin type are heat treatable has been known since the investigations of Wilm in 1903, and the phenomena involved are common to many alloys. In a general way, the heat treatability of aluminum alloys is owing to the varying solubility of metallographic constituents with temperature, *e.g.*, CuAl<sub>2</sub> in aluminum-copper alloys and duralumin and Mg<sub>2</sub>Si in duralumin. When such alloys are heated to moderately high temperature, *e.g.*, 500°C., more of the constituents go into solution, and, when quenched, these constituents at first remain in solution but on standing precipitate out in particles of very high dispersion. Consequently, hardening and strengthening ensue.

Worked aluminum and aluminum alloys are softened by simple anneal at 350 to 500°C., depending upon the amount of reduction and the time period of anneal. Certain cast aluminum alloys, *e.g.*, 95:5 aluminum-copper alloy, are suitable for quenching heat treatment, and this is now being employed somewhat in practice for enhancing the properties of sand castings. The strength of the rolled and annealed 95:5 aluminum-copper alloy is increased from about 27,000 to 52,000 lb. per square inch by quenching and aging. When duralumin is quenched from about 500°C., it is soft and ductile, but on aging at the ordinary temperature for a few days the hardness and strength increase markedly while the elongation falls off. The aging may be accelerated by heating at 100 to 200°C. for 1 to 5 hrs. The heat treatment of duralumin has been discussed by a number of workers, including Merica and his collaborators,<sup>61</sup> Hanson,<sup>64</sup> Rosenhain<sup>65</sup> *et al.*, Konno,<sup>76</sup> Knerr,<sup>64</sup> and many others. The hardening and strengthening on heat treatment is due to the precipitation of CuAl<sub>2</sub> and Mg<sub>2</sub>Si. In practice, heat treatment is applied principally to worked duralumin, and the heating is carried out under careful pyrometric control in any suitable furnace. The quenching medium may be cold water, boiling water, or oil. Parts may be heated for quenching in a salt bath, *i.e.*, a mixture of potassium and sodium nitrates. Since quenched duralumin is soft, the material may be quenched in water, then immediately worked to the required shape, and then allowed to age. Zinc duralumin is heat treatable, as is the 92.5:4:1.5:2 aluminum-copper-magnesium-nickel alloy. Heat-treated duralumins have been used very largely in aircraft construction, but they are being employed to an increasing extent in the automotive industry and the general engineering trades.

**Soldering and Welding.**—The soldering of aluminum and aluminum alloys has attracted a great deal of interest on the part of laymen, and many patents have been taken out for solders and soldering fluxes purported to be suitable for joining aluminum and aluminum-alloy parts. Most of these are entirely useless.

Aluminum parts can be soldered together fairly easily, provided the proper precautions are taken, but in all cases, irrespective of the solder employed, the joint is not permanent and fails after a short time on exposure to moisture or humid atmospheres. Joints fail because all the metals used in solders are electronegative to aluminum, and in the presence of water galvanic couples are formed, so that disintegration takes place by electrolytic corrosion. Soldering should never be done if the joint is to be exposed to moisture or if it must withstand stresses. Soldering may be regarded as satisfactory if it is desired simply "to stick parts together" and no permanence is required. While welding is the only method to be recommended for joining aluminum and aluminum-alloy parts where the joint is exposed to the weather or must be strong, still in practice it is often desired to solder, *e.g.*, in repairing slight defects in castings or in making small repairs on aluminum parts. The essential features of soldering and welding are discussed briefly below.

The limitations of soldering aluminum and its alloys have been thoroughly discussed,<sup>30, 54, 109</sup> and soldering should certainly have very limited application in aluminum work, and it never should be used for the assembly of structures. Aluminum solders usually consist of low-melting-point alloys of zinc, tin, and aluminum, although many complex alloys have been suggested, containing copper, lead, iron, bismuth, antimony, and other metals in addition. The function of metals other than zinc, tin, and aluminum in a solder is not clear, and practically any other added metal is of no use, if not harmful. Most commercial aluminum solders that are useful contain 40 to 80 per cent tin, 10 to 50 per cent zinc, and 0 to 10 per cent aluminum, and the melting range is about 200 to 500°C. Their strength is 6,000 to 14,000 lb. per square inch and elongation 2 to 20 per cent. A ductile solder is desirable, and the presence of copper or antimony, or excess of aluminum, which causes brittleness, is to be avoided. Normally, the strength of soldered joints is not equal to the strength of the solder, and failure may occur through the solder and at the joint on breaking.

While various fluxes are recommended for soldering, these are quite unnecessary, and soldering may be conveniently carried out as follows: The surfaces to be soldered are carefully cleaned with a file or emery paper, and are then "tinned" or coated with a layer of the solder by heating the surface and rubbing the solder into it. The joint between the "tinned" surfaces is then made in the ordinary way with a soldering iron and the solder. In giving the preliminary coat of "tin" to the surface, the solder may be rubbed in thoroughly with a wire scratch brush. Soldering may also be carried out by first electroplating the surfaces, and the joint depends upon the firmness with which the electrodeposited metal adheres to the aluminum. Copper plating is sometimes used. Where soldering is done directly without electroplating, the effectiveness of the joint depends upon the adhesion between the aluminum and the initial layer of solder.

As indicated, the applications of soldering to aluminum and its alloys are limited. Soldering should never be used for structural assembly, but it is useful for making repairs on defective castings in the foundry,<sup>109</sup> *e.g.*, in filling up small holes, blows, draws, etc. It should not be applied in building up large bosses or lugs, but is not dangerous for patching small defects that mar the appearance of an otherwise good casting. The best solders are tin-zinc and tin-zinc-aluminum alloys; in the former, the composition is 15 to 50 per cent zinc and the remainder tin, and in the latter the composition is 5 to 12 per cent aluminum, 8 to 15 per cent zinc, and the remainder tin.

Autogenous welding by an oxygen method is employed extensively in the aluminum industry for making joints of substantially pure aluminum and aluminum alloys, for the assembly of structures, and for making repairs and salvaging castings. Aluminum

sheet is welded in building up tanks and vessels for the chemical industry, and when sheets are joined, butt welding by the oxyacetylene or other oxygas process is suitable except in very light gage sheet where the edges are lap or flange welded. The oxygas process of welding the light aluminum alloys causes actual alloying of the parts to be joined and the welding material, and a fairly solid alloy can be obtained at the juncture if proper precautions are observed. In the assembly of structures, a number of methods, such as riveting, folding, sewing, doweling, and the like, have been replaced by welding. Autogenous welding consists in heating the two parts to be joined and then running liquid metal in at the juncture. In welding aluminum, it is useful to use an aluminum wire as the welding material, while for the light alloys a stick or rod of the same composition as the alloys is employed. In welding, the principal difficulty encountered is the removal of the aluminum oxide from the surfaces to be joined and in practice this is accomplished by chemical (fluxes) or mechanical (puddling) means. Electric-resistance and electric-arc welding are used for aluminum and its alloys in addition to the oxygas process.

Many salts and mixtures of salts have been suggested for welding fluxes, but a flux that will dissolve aluminum oxide is required. The most suitable fluxes are mixtures of alkali fluorides and chlorides as patented by Schoop.<sup>1</sup> A good flux for welding consists of 0.124 lb. potassium carbonate, 0.33 lb. lithium fluoride, 2.53 lb. sodium chloride, and 3.0 lb. potassium chloride. While fluxes are generally used in welding aluminum, they are not favored in American practice for repairing castings, and in such work the aluminum oxide film is broken down mechanically by a puddling rod. Oxyhydrogen and oxyacetylene welding is done on both aluminum and its alloys, and the former is probably preferable. In welding aluminum sheet, *e.g.*, building tanks, butt welding is suitable and a feeder of aluminum wire is used. The surfaces to be joined are heated, and the wire covered with flux is melted in the torch and run into place, being puddled down and smoothed off. Welding thin stock requires considerable skill.

The repair of aluminum-alloy castings is usually done by oxyacetylene welding, using no flux and a welding stick of the same composition as the castings. For small welds, the casting should be preheated with the torch over a considerable area in the vicinity of the spot to be welded, but for large welds and even small welds on complicated castings it is best to heat the entire casting to 300 to 450°C. in a preheater. The stock in the vicinity of the place to be welded is melted down with the torch, and the hole so made is filled with liquid alloy from the welding rod, also melted by the torch. The metal is then puddled and poked with an iron rod until a pool is formed which insures thorough alloying with the body of the casting. The operation should be conducted rapidly, and excess alloy is scraped off while still pasty. Large castings should be cooled slowly in the furnace or in hot ashes after welding to avoid cracking. Heat-treated duralumin parts are welded in aircraft assemblies, and such welds should be heat treated.

**Stamping, Pressing, Machining, and Finishing.**—Aluminum and its light alloys are fabricated into various objects by stamping, pressing, drawing, and spinning. Considerable amounts of aluminum sheet are fabricated into cooking utensils by pressing, drawing, and spinning, and many small articles are made by light stamping. In draw-press work, annealed aluminum sheet stock, usually circle forms, are drawn into hollow shapes, and these may subsequently be spun on lathes around a mandrel. Iron or wooden chucks are employed and the spinning speed is 1,500 to 2,500 r.p.m. or more. Intermediate annealing may be necessary for very heavy stamping and draw-press work. Aluminum and aluminum-alloy

<sup>1</sup> U. S. Patent 922523, May 25, 1909; English Patent 24283, Nov. 2, 1907; and other patents.

sheet is bent, shaped, and formed in making motor-car bodies, fenders, aircraft fuselages, and other structures, and the materials may be pressed in draw presses or hammered over forms. In finishing aluminum and light alloy manufactures, parts may be polished, scratched, or colored. In polishing, the materials are first buffed on sewn rag buffs glued together to form wheels, and a fine abrasive is applied with oil. Final polishing is done with tripoli or special polishing powders on cotton-rag wheels. Aluminum may be given a frosted finish by scratching on a wheel made of fine wires. Dip finishes are given by immersing in 15 per cent sodium hydroxide in aqueous solution followed by washing in water, and then dipping in nitric acid; the part is then again washed and dried. Aluminum may be colored by special treatments with chemical reagents, giving bronze and other color effects to the surface. For painting, aluminum and its alloys are prepared by sand papering followed by sand blasting or by scratch brushing.

Substantially pure aluminum does not machine well owing to its softness and toughness, and it drags and tears under cutting tools. Most of the useful light alloys, however, can be fairly readily machined. A lubricant is necessary and advisable for many operations. A few of the lubricants employed in American machine shops include crude oil, kerosene, soapy water, paraffin oil, mixtures of oils, such as 70 per cent kerosene and 30 per cent lard oil, and water-oil emulsions. Lubricants need not be used on roughing cuts unless very heavy, and kerosene is much employed for machining cuts. Machining speeds and feeds are very variable. In rough turning on cast aluminum alloys, the roughing-cut speed may be 400 to 700 ft. per minute under feeds of  $\frac{1}{16}$  to  $\frac{5}{32}$  in., depending upon the work; 500 ft. per minute is a fair roughing speed with  $\frac{1}{8}$ -in. feed. In finish turning, the speed may be 125 to 175 ft. per minute and 140 ft. is a fair speed. In roughing, milling cutters may be run at 300 r.p.m. and a feed of 14 in. per minute, removing  $\frac{3}{16}$  in. of stock. For finishing, milling cutters may be run at 275 r.p.m. and a feed of 13 in. per minute, removing  $\frac{1}{32}$  in. of stock. In drill-press operations, on boring holes  $\frac{1}{4}$  to  $\frac{1}{2}$ -in. diameter, the drills may run at 1,200 r.p.m. and a feed of 0.002 in. per revolution. Aluminum alloys can be finished nicely by grinding, *e.g.*, for pistons; a No. 40 grain Crystolon wheel, in J or K grade is suitable, and the lubricant may be 10 per cent lard oil and 90 per cent water.

The cutting tools for machining aluminum and its alloys may be either ordinary high-carbon steel or high-speed steel. Tools should be made very sharp and pointed and have large rakes and clearances. In boring, the tool should be set just below the center of rotation of the work, and in turning, just above. In general, the speed should be as high as can be run with the work and alloy in hand, the limiting factors being the mode of holding the work and arranging it so as to withstand the cutting stresses without distortion. For turning, a lathe tool should have a top rake at an angle of 25 to 30 deg. to the right and about 15 deg. back. The forward or cutting corner should be well rounded to say about  $\frac{1}{16}$ -in. radius. The face of the tool need not be ground with a great deal of clearance, and this may be about 10 deg. with the vertical. In general, aluminum alloys can be cut at about four times the speed and twice the feed possible with mild steel.

The electroplating of aluminum and its alloys is of some importance commercially, but not much success has so far been attained in electroplating the metal. The principal difficulty comes in securing a satisfactory deposit that will not strip or flake off. Moreover, it is necessary to remove the oxide film on aluminum before plating, and to overcome the deposition that takes place on immersion in a plating bath. There are very many patented processes for plating, but these cannot be considered here. A successful method for nickel plating is said to have been developed by Ledin,<sup>90</sup>

which entails the following: The parts to be plated are first cleaned, then dipped in concentrated hydrochloric acid, then dipped in a cadmium chloride bath (made up of 100 c.c. hydrochloric acid, 400 c.c. water, and 9 g. cadmium chloride), and then plated. The plating bath is made up to contain 50 g. nickel sulphate and 35 g. sodium citrate per liter of water, and deposition is made with current density of  $\frac{1}{2}$  amp. per square decimeter.

**Selected Bibliography.**—The technical and scientific literature relating to aluminum and aluminum alloys is very extensive, and many papers have been published recently dealing, in particular, with the metallurgy of the alloys. A comprehensive text book on the subject has been prepared by the writer,<sup>18</sup> there are several old texts dealing with the metal, and several short books dealing with certain aspects of the subject have appeared in recent years. An excellent short summary on aluminum and its alloys is given in *Circ. 76* of the U. S. Bureau of Standards. A review of the aluminum industry is published annually in "Mineral Resources of the United States" by the U. S. Geological Survey. For many years, the late lamented Dr. J. W. Richards contributed the chapter on aluminum to "The Mineral Industry," published annually by the McGraw-Hill Book Co., Inc., and this has been continued since his death by the present writer. These reviews are of interest in reflecting the yearly developments in the industry and give current information on aluminum, aluminum alloys, and bauxite, as well as many references. Valuable information on the metal and its alloys is to be found, particularly in the *Journal* of the Institute of Metals, *Revue de l'Aluminium*, *Révue de Metallurgie*, *Zeitschrift für Metallkunde*, the *Transactions* of the American Foundrymen's Association, and the *Transactions* of the A. I. M. M. E. In the United States, reports of investigations on aluminum and aluminum alloys are issued periodically by the U. S. Bureau of Mines and the U. S. Bureau of Standards. In England, the reports by the Alloys Research Committee of the Institution of Mechanical Engineers, emanating from the National Physical Laboratory (Teddington), are most valuable.

Several extensive bibliographies on aluminum and aluminum alloys have been published, and following are a few selected references to some of the more important publications on the subject. These will serve as a guide to the literature.

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## CHAPTER XX

### METALLURGY OF MAGNESIUM AND MAGNESIUM ALLOYS

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**Introductory.**—Magnesium is the leading member of the alkali-earth division of the second group and is the lightest metal now employed for engineering purposes of construction. Its specific gravity is 1.74. The technical metallurgy of magnesium is similar to that of aluminum, and cheap electric power is necessary to its commercial production. Magnesium was little known and used in the United States prior to 1914, and important production of the metal began here in 1915 when imports, which came largely from Germany, were cut off. While actual consumption of magnesium and its alloys for engineering purposes has so far been small, development in the production of castings and wrought shapes has been very rapid in the past few years, and with sufficient reduction in price a greatly increased use of the metal and its light alloys may be expected. In Germany, magnesium has assumed first-rate importance, being a competitor of aluminum in several lines. While domestic production was substantial during the period 1915 to 1919, the industry slumped markedly during the years 1920 to 1922 inclusive. In the past three years, production has again gradually increased owing to gradually increased use of the metal and its alloys in the engineering field. Eventually, the magnesium industry in all producing countries is expected to develop along the same lines as the aluminum industry.

**Historical Survey.**—In 1808, Davy first made magnesium by the reduction of magnesium oxide with potassium vapor and also by the electrolysis of anhydrous magnesium chloride, but the metal obtained was very impure. In 1830, Bussy made magnesium by reduction of anhydrous magnesium chloride with potassium, and in 1852 Bunsen prepared it by electrolysis of the anhydrous chloride in a porcelain crucible using carbon anode and cathode. In 1856, Matthiessen produced the metal by electrolysis of a liquid (fused) mixture of magnesium chloride and potassium chloride (4:3) plus a little ammonium chloride. The first industrial production was undertaken in France by Deville and Caron in 1863. Their process entailed reduction of a mixture of anhydrous magnesium chloride and calcium fluoride by metallic sodium, using closed iron crucibles as the containing vessels. Deville showed also at this time that magnesium could be distilled in an atmosphere of hydrogen, and he prepared very pure metal by this process.

Later, Sonstadt introduced improvements in the Deville-Caron process, whereby the metal was made by reduction of a mixture of magnesium chloride and sodium chloride with sodium in iron retorts, followed by distillation of the resulting impure metal. In 1885, von Püttner produced magnesium by a process closely resembling zinc retorting. In the process, a magnesium mineral (*e.g.*, magnesite) is first converted to the oxide, and this is reduced by carbon in heated retorts, the reduced magnesium

<sup>1</sup> Consulting Metallurgical Engineer, Cleveland, Ohio.

distilling and being condensed. A number of patents were taken out after 1880 for processes specifying electrolysis of magnesium salts, both aqueous and fused, and for the reduction of magnesium compounds to metal by carbon, aluminum, etc., but these cannot be considered here. In the ordinary electrolytic process which was developed in Germany and which supplanted Sonstadt's method, an anhydrous fused electrolyte having the composition  $\text{MgCl}_2 \cdot \text{KCl} \cdot \text{NaCl}$  (or other mixture of the three chlorides) is electrolyzed in iron cells using carbon anodes, the iron of the cells forming the cathode. In this process, the magnesium is dissociated by the current, floats on top of the bath, and is ladled off. This was the principal process employed in Germany prior to the war, and the same process or a modification thereof is now employed by several producers. In more recent years, a process calling for the electrolysis of magnesium oxide dissolved in a fluoride bath has been developed; this is analogous to the Hall-Héroult process for the production of aluminum.

**Producers and Output.**—The world's magnesium industry is small, and the total output probably never exceeded 5,000,000 lb. per annum, although statistics as to foreign production have never been made available. As indicated domestic production was the direct result of the war, and magnesium had not been used in the United States prior to 1914 except for photographic flashlights and for experimental purposes. Magnesium was first made in the United States by a company in Boston, Mass., using the Sonstadt method, but the amount produced was not large. This company apparently was in existence over the period 1865 to 1892. Referring to more recent years and to quantity production by modern methods, the first American production was probably by the Cunniff brothers (the Rumford Metal Co.) at Rumford Falls, Maine, in 1914–1915, and in 1915 production began on a fairly large scale in the United States, France, and England. Among former producers in the United States may be mentioned the Electric Reduction Co., Washington, Pa.; the General Electric Co., Schenectady, N. Y.; the Norton Laboratories Co., Lockport, N. Y.; and the Aviation Materials Co., Niagara Falls, N. Y.

At the present time, the domestic producers of magnesium and magnesium alloys are the Dow Chemical Co., Midland, Mich., and the American Magnesium Corporation (a subsidiary of the Aluminum Co. of America), Niagara Falls, N. Y. Magnesium has been made in Canada by the Shawinigan Electro-Metals Co., Ltd., Shawinigan Falls, P. Q. The English producer is the Magnesium Co., of Wolverhampton, while production in Germany is controlled by the Chemische Fabrik Griesheim-Elektron. In 1921, the Aktieselskabet de Norske Saltverker started the erection of a factory at Fjotlandsvaag, Norway. During the war, production was undertaken in France by the Société d'Electrochimie et d'Electrometallurgie at Clavaux (Isère). There has, of course, been small and sporadic production of magnesium in most consuming countries for many years, but the principal producer has been Germany.

Table 1 gives the domestic production over the period 1915 to 1924, and imports over the period 1918 to 1924 are shown in Table 2. Prior to the war, domestic imports were at the rate of 35,000 lb. per annum; exports have been negligible.

**Markets and Prices.**—Since magnesium is relatively new commercially, its marketing has been, except in Germany, more in the direction of introductory selling. The market for the metal has been strictly limited owing to the high price, but a general schedule of prices for various forms has been drawn up. In 1883, the price of magnesium in Europe was about \$32 per pound, while in 1902 it had dropped to about \$3. The price in the United States before the war was about \$1.45, but during the war it rose to as high as \$10, while now (1925) it has been quoted as low as 75 cts. per lb. in ton lots for pig (cf. also Table 1). In Germany, the price has been under 40 cts. recently, and the metal consequently is a strong competitor for aluminum. The present import duty into the United States on metallic magnesium and magnesium scrap is 40 cts. per pound, and on magnesium alloys, powder, sheet, wire, ribbon, and other manufactures is 40 cts.

per pound on the magnesium content and 20 per cent *ad valorem*. At present, magnesium-base alloy castings cost \$2 to \$4 per lb. depending on the size and design. Colby<sup>32</sup> discusses<sup>1</sup> the prices of various commercial forms of magnesium. It should be pointed out that transportation rates on the metal are high, double first class being the tariff. One domestic producer looks for 50 ct. metal in the future.

**Magnesium Sources, Ores, and Minerals.**—The ores, or raw materials, for the production of magnesium are extremely abundant, and magnesium is fifth in abundance of the metals in the earth following silicon, aluminum, iron, and calcium in the order named. Magnesium constitutes 2.24 per cent of the earth's crust (Clarke). Unlike aluminum-mineral deposits which are found only fairly frequently in suitable composition and tonnage for the production of aluminum by electrolytic processes, magnesium deposits, notably magnesite and dolomite, occur in large amounts, widely distributed, and of suitable quality for magnesium production. Magnesium salts, notably the chloride, double chlorides, and sulphate, are found in salt beds, and are constituents of saline springs, salt lakes, and the ocean.

Magnesium is never found native. Some important magnesium minerals include magnesite ( $\text{MgCO}_3$ ), dolomite ( $(\text{MgCa})\text{CO}_3$ ), kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ), kainite ( $\text{MgSO}_4 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ ), carnallite ( $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ ), brucite ( $\text{Mg}(\text{OH})_2$ ), spinel ( $\text{MgAl}_2\text{O}_4$ ), serpentine ( $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_{10}$ ), and talc ( $\text{H}_2\text{Mg}_3\text{Si}_4\text{O}_{12}$ ). In igneous rocks, magnesium is represented by amphiboles, micas, pyroxenes, and olivine. Talc, chlorite, and serpentine are common magnesium silicates, and dolomite is frequently found in enormous mountain masses. Magnesite is mined in Australia, Austria, Hungary, Czecho-Slovakia, British India, Canada, Greece, Italy, Spain, South Africa, and in the Pacific coast states of California and Washington, U. S. A. Dolomite is mined in California, Colorado, Illinois, Ohio, Pennsylvania, and West Virginia, and various foreign countries. The sulphate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) is one of the principal saline constituents of many springs. There is a peculiar deposit of pure magnesium sulphate at Basque, B. C., and this salt is obtained commercially from a dry-lake deposit near Oroville, Wash., and from the bitterns of certain Californian salt works. On the rain-protected cliffs at Korpklint, in Gottland, occur chalk-white efflorescences of magnesium sulphate, apparently exuded from the rocks.

In oceanic salts, magnesium chloride makes up about 11 per cent of the total salt content, and oceanic water contains about one-eighth per cent magnesium. Magnesium-bearing bitterns are found at San Mateo, Cal.; Syracuse, N. Y.; Pomeroy, Ohio; Hartford, W. Va.; in the Saginaw Valley of Michigan, notably at Midland; in Colombia; in Germany; and elsewhere. The magnesium content of some inland salt lakes is high, notably Great Salt Lake, Utah, which contains 0.56 per cent magnesium. Houghton Lake, at Dana, Saskatchewan, is underlain by a 1-ft. thick layer of salts, chiefly magnesium sulphate and sodium sulphate. The principal and most famous salt-bed deposits containing magnesium minerals are the great Stassfurt salt beds in Germany (Magdeburg-Halberstadt region). The principal magnesium-bearing minerals of these beds are carnallite ( $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ ), bischofite ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), and tachydrite ( $2\text{MgCl}_2 \cdot \text{CaCl}_2 \cdot 12\text{H}_2\text{O}$ ). Magnesium-bearing salt beds also occur in Spain and Alsace.

While minerals and ores of magnesium are abundant, in practice raw materials for production of the metal are obtained from only a few sources. These are: anhydrous

<sup>1</sup> Throughout this chapter reference numbers apply to appended bibliography except in the case of obvious footnotes.

sodium magnesium chloride, left after extraction of salt and bromine from brines at Midland, Mich.; carnallite from Stassfurt; magnesite (notably from California); and magnesium carbonate, precipitated from dolomite. Magnesium has been made experimentally from magnesium chloride obtained from sea water, and some producers have employed the chloride obtained by chlorination of the oxide. Except for about two years, the supply of magnesium chloride in the by-product bitterns from the solar evaporation of salt along the shores of Great Salt Lake and the Californian coast has practically all been discarded. Bitterns made from sea water at various points around San Francisco Bay, California, carry 2.3 to 8.6 per cent magnesium. Magnesium chloride is a by-product of the preparation of magnesium salts in Germany and can be made very cheaply there. The magnesium content of magnesite averages 25 per cent and that of carnallite 8 per cent.

**Production of Magnesium.**—Many processes for the production of magnesium have been patented, suggested, or actually used commercially. All these cannot be taken up here, but the following type processes may be mentioned: (1) reduction of magnesium compounds by a metal, *e.g.*, reduction of anhydrous fused magnesium chloride with sodium, or of magnesium oxide with aluminum; (2) reduction of magnesium compounds by carbon, *e.g.*, magnesium oxide, followed by sublimation and condensation of the metal in a manner similar to zinc retorting; (3) electrolysis of anhydrous magnesium chloride or a mixture of magnesium chloride and another chloride (sodium or potassium chloride, or both) in the fused condition; (4) electrolysis of magnesium oxide dissolved in a suitable fused bath, *e.g.*, in magnesium fluoride, in a manner similar to the Hall-Héroult aluminum process; (5) electrolysis of aqueous solutions of magnesium salts; (6) electrolysis of magnesium sulphide in a suitable fused bath.

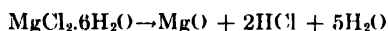
The first process, *i.e.*, reduction of magnesium chloride by sodium, has been used commercially, but it is quite out of the question for commercial production now, involving as it does the use of electrolytic sodium. The second process, involving carbon reduction, has been used commercially and is a sound method, although not now employed. The third process, *i.e.*, electrolysis of fused salt mixtures high in anhydrous magnesium chloride, is the usual one employed at the present time, and this process is used by the Dow Chemical Co., the Chemische Fabrik Griesheim-Elektron, and the Magnesium Co. The fourth process is analogous to the present aluminum reduction process and has been developed and employed by the American Magnesium Corporation. The fifth process is technically unsound because of the high electrolytic-solution pressure of the metal ( $E_h = +1.55$  volts). The sixth process is feasible but has not been used commercially.

At the present time magnesium is made by two different processes, *viz.* (1) electrolysis of anhydrous magnesium chloride in admixture with potassium chloride or sodium chloride, and (2) electrolysis of magnesium oxide dissolved in a fused bath of magnesium fluoride (plus other added salts). The production of magnesium has been described in published papers by Tucker and Jouard,<sup>2</sup> Grosvenor,<sup>4</sup> Phalen,<sup>10</sup> Flusin,<sup>14</sup> Allen,<sup>18</sup> Boyton and his co-workers,<sup>20</sup> Fedotieff,<sup>24</sup> Miyake and Butts,<sup>38</sup> Harvey,<sup>40</sup> and others, and in many patents, *e.g.*, those of Ashcroft, Seward, Backer, and Harvey (*vide below*).

**Magnesium Chloride Process.**—The magnesium chloride process for the production of metallic magnesium involves three steps, *viz.*, (1) preparation of

anhydrous magnesium chloride as such or in admixture with alkali chlorides; (2) electrolysis of the magnesium chloride in a cell at low voltage; and (3) purification of the resulting metal. In employing hydrous magnesium chloride as the raw material, the water must first be removed, and it should be stated at the outset that the anhydrous salt cannot be produced directly by heating the hydrous material.

When aqueous solutions of magnesium chloride are evaporated and crystallized the salt obtained is  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . If this salt is heated, it melts in its water of crystallization, and the reaction



takes place, so that the final product is magnesium oxide. The complete dehydration of hydrous magnesium chloride has been made the subject of many patents, and the usual methods employed entail heating the crystallized  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  in admixture with alkali chlorides or in a current of chlorine or hydrochloric acid gas. Thus, in a process of the Dow Chemical Co., the hydrous chloride is first heated<sup>10</sup> at low temperature in admixture with 25 per cent sodium chloride plus a small amount of ammonium chloride, whereby about 50 per cent of the water is driven off. The partly dried mix is then cooled and reheated at higher temperature until the remaining water is removed. In the process of the Magnesium Co., the hydrous chloride is heated<sup>18</sup> for several hours at 150°C. in dry air; part of the water is driven off, yielding a product of the composition 73 per cent  $\text{MgCl}_2$ , 4 per cent  $\text{MgO}$ , and 23 per cent  $\text{H}_2\text{O}$ . This material is then reheated in a current of hydrochloric acid gas at 300°C., whereby the remaining water is removed, the magnesia converted to magnesium chloride, and a product containing 99+ per cent of magnesium chloride obtained. Recovery of chlorine is made in the Dow process and of hydrochloric acid in the process of the Magnesium Co. In all processes devised for the production of anhydrous magnesium chloride, the object in view is to prevent conversion of the chloride to oxide on heating. Bailey and Foster<sup>1</sup> have patented a process for making anhydrous magnesium chloride in which magnesium carbonate, or oxide, is chlorinated in the presence of carbon, and similar processes have been patented by Ashcroft<sup>2</sup> and by the Aktieselskabet de Norske Saltværker.<sup>3</sup> A process for the preparation of magnesium chloride from dolomite has been patented by Barstow<sup>4</sup> and one for the recovery of the salt from brines by Dow and Barstow.<sup>5</sup> Other patents for the preparation of anhydrous magnesium chloride include those of Bull,<sup>6</sup> Namari,<sup>7</sup> Collings and Gann,<sup>8</sup> and Goldschmidt.<sup>9</sup>

After preparing anhydrous magnesium chloride or a suitable mixture of this salt with alkali chlorides, the material is electrolyzed at 675 to 725°C. in a suitable cell. Although the decomposition voltage of magnesium chloride is only 3.25 volts, about 5 to 8 volts are required in practice. In the process, anhydrous magnesium chloride is added to the bath from time to time as electrolysis proceeds in order to keep the bath within the required working limits of composition. Where renewal of the magnesium chloride is not made, a batch process results, and it is preferable to make the operation

continuous. Various types of cells are employed. In a single-stage operation the cell is a cylindrical or rectangular iron box having carbon anodes, the iron of the cell serving as the cathode. In some cells, a cathode of steel may be suspended in the bath. The cell is heated externally in starting the process, but after electrolysis begins no further external heating is necessary, since the imposed current serves both for electrolytic dissociation of the salt and for maintaining the temperature of the bath. During electrolysis the metal collects at the surface of the cathode in the form of small globules; these gradually grow larger with further deposition of metal and finally detach from the electrode, rising to the surface, where they float. The chlorine is liberated at the anode and is swept out of the cell and recovered. The magnesium is ladled out of the cell from time to time and cast into crude ingots, or is ladled directly into iron pots for purifying. The metal is fluxed in the pots with fused sodium magnesium chloride and cast into ingots or sticks. A small cell taking a 100-lb. charge yields

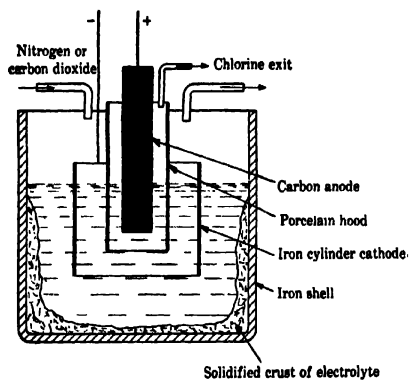


Fig. 1.—Cell for magnesium production from magnesium chloride. (Rideal.)

26 to 28 lb. of metal per 24 hr. Figure 1 shows a form of cell in which a porcelain hood is placed in the bath to keep the floating magnesium from contact with the anodically separated chlorine. In this cell, nitrogen or carbon dioxide is used to sweep out any chlorine that may penetrate to the cathode compartment. The chlorine from the anode is aspirated through the pipe shown and recovered.

The Magnesium Co., of Wolverhampton, England, employs<sup>18</sup> a two-stage process in order to avoid the use of a diaphragm or partitioned cell. The cell is of cast steel with a fire-brick lining, fitted with a gas-tight cover carrying graphite anodes and means for outlet of the chlorine. The cell is charged with liquid lead for the cathode, and this is covered with the electrolyte into which the anodes dip. Means are provided for circulating both the bath and the lead cathode. The cell has capacity of 5,000 amp. at current density of 1,500 amp. per square foot with voltage drop of 5 at the terminals. The cell is self-heating and produces about 100 lb. of magnesium per 24 hr. as a lead-magnesium alloy, with current efficiency of 85 per cent. The first operation is the electrolysis of the magnesium chloride electrolyte so as to produce a magnesium-lead alloy at the cathode, and in the second stage this alloy acts as the anode in another cell and the cathode consists of a large number of steel rods immersed in the magnesium chloride electrolyte. The second cell is operated in series with the first at 5,000 amp. and a voltage of 2. The total energy consumption is 8.5 kw.-hr. per pound of magnesium produced. The chlorine is aspirated from the cells to scrubbing



towers and absorbed in milk of magnesia with the formation of magnesium chloride and chlorate, with subsequent recovery of the chlorate as  $\text{KClO}_3$ ; the magnesium chloride is returned to the process.

Various patents have been taken out for the production of magnesium by the electrolysis of magnesium chloride, particularly by Ashcroft,<sup>1</sup> Hutchinson,<sup>2</sup> and Backer.<sup>3</sup> Dantsigen<sup>4</sup> specifies the electrolysis of a mixture of magnesium chloride and potassium chloride plus calcium fluoride in a cell, using carbon anodes and sherardized iron, copper-coated iron, or tin-coated iron for the cathodes. In a patent by Seward and von Kugelgen,<sup>5</sup> a process is specified for the electrolysis of the mixed chlorides over a bath of tin or copper as the cathode. In a patent by Iwahashi and Kishimoto,<sup>6</sup> an alternating current of suitable current density is passed into magnesium chloride in a cell using graphite or carbon as anode and iron as cathode; the water in the chloride is evaporated, and the salt said to be fused without decomposition; after the fused salt ceases to bubble, it is electrolyzed by direct current.

**Magnesium Oxide Process.**—A process for the production of magnesium that is analogous to the Hall-Héroult process for the reduction of aluminum has been patented by Seward<sup>7</sup> and by Harvey<sup>8</sup> and is used by the American Magnesium Corporation. In this process, substantially pure magnesia ( $\text{MgO}$ ) is dissolved in a liquid (fused) electrolyte, consisting of about equal parts of magnesium fluoride and barium fluoride plus sufficient sodium fluoride to give the required fluidity, and electrolyzed. The magnesia is prepared by the calcination of magnesite obtained from the Pacific coast and shipped to the works at Niagara Falls, N. Y. (In an older patent by Seward and von Kugelgen,<sup>9</sup> a process was patented for the production of aluminum-magnesium alloys by electrolyzing magnesium oxide dissolved in magnesium fluoride plus lithium fluoride, using liquid aluminum as the cathode.) The magnesium-oxide process is discussed by Harvey.<sup>40</sup>

The cell or furnace used in the magnesium oxide process may be conveniently described by reference to Figs. 2 and 3. The former shows a transverse section of the furnace and the latter is a plan. In the figures, 1 is a wrought-iron vessel supported on blocks 2, and 3 represents the solidified portion of the bath 4. The cathodes are represented by 5, which consist of iron or steel castings extending longitudinally through the furnace and projecting through apertures 6 in the bottom. A layer of asbestos 20 is placed between the cathodes and the furnace shell. The anodes are shown at 9, and these are of graphite or carbon, suspended in the bath. A layer of magnesium oxide 10 is maintained on top of the bath as a source of raw material. Cooling pipes 11 are arranged between the cathodes and anodes so as to cause solidification of a portion of the bath to form vertical partitions of insulating material. Hoods or collecting chambers are shown at 12 receiving the liquid magnesium which ascends from the cathodes: these chambers are made of cast or sheet-metal casings 13 placed near the surface of the bath and suitably cooled. They are shown as supported

from the upper edges of the side walls of the furnace shell 1. The inner wall 14 of each hood is situated sufficiently close to the cooling pipes 11 so that the mass of solidified salts extends to the wall 14 and seals the space between the wall and the pipes. The liquid metal collected in the hoods or chambers may be drawn off continuously or

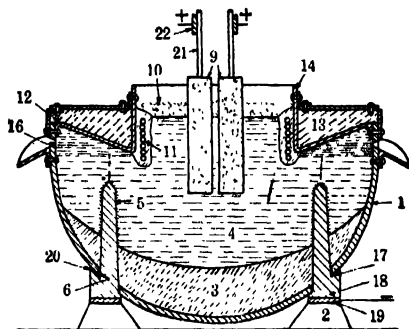


FIG. 2. —Magnesium reduction furnace. (Seward.)

tapped intermittently from tap holes 16. The cathodes 5 are formed with shoulders 17 for receiving the weight of the furnace, and have flat bottoms 18 which rest on flat copper bus bars 19. The anodes are carried by rods 21 and fastened to bus bars 22. In operation of the process, the bath is maintained at about 950°C. and its specific

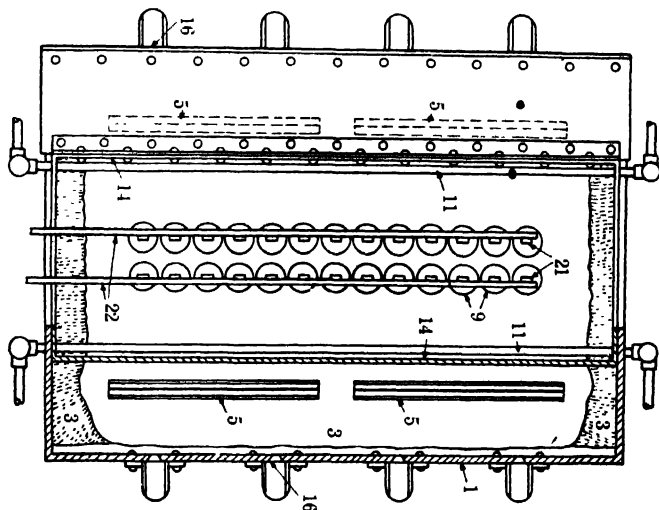
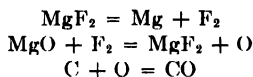


FIG. 3. —Plan of magnesium-reduction furnace. (Seward.)

gravity at about 3.2. The magnesium oxide is added to the bath around the anodes at frequent intervals. The current may be 9,000 to 13,000 amperes at an e.m.f. of 9 to 16 volts. The average current efficiency may be taken as 50 per cent with a power efficiency of 40 per cent. The dissociated oxygen burns at the carbon anodes, the

magnesium is liberated at the cathodes and rises into the collecting chambers from which it is removed. The metal is refined by remelting with a flux, and specially pure metal is prepared by volatilizing the crude magnesium and condensing it.<sup>1</sup>

Magnesium oxide is only slightly soluble in the fluoride bath—in which respect it differs considerably from aluminum oxide—the solubility being only about 0.1 per cent. Strictly speaking, therefore, the process is probably not a direct electrolysis of the oxide. It has been suggested that the mechanism is as follows:

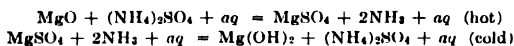


**Commercial Forms of Magnesium.**—Substantially pure magnesium is supplied to the trade in the form of sticks, ingots, blocks, rods, bars, tubes, sheets, plate, wire, powder, foil, and ribbon. Powder is made 40 to 200 mesh, depending upon requirements. For deoxidizing, the metal is furnished as sticks or in the form of extruded ingot with diameter of about  $1\frac{1}{4}$  in. Flash light powder usually runs 100 to 150 mesh, while powder for signal lights in marine and military work is usually 50 mesh. Sheet and plate are available from  $\frac{3}{4}$  in. thick up to No. 30 B. & S. gage, while rod is produced from  $\frac{3}{8}$  to  $1\frac{1}{4}$  in. Tubing is made up to  $1\frac{1}{4}$  in. outside diameter, and wire is furnished from No. 36 to No. 00 B. & S. gage. Ribbon is usually made  $\frac{1}{8}$ -in. wide by 0.006-in. thick. Sand and permanent-mold castings are made in both magnesium and its light alloys. The usual grades of stick and ingot metal are as follows: No. 0, containing 99.99 per cent Mg minimum; No. 1, containing 99.85 per cent Mg; and No. 2, containing 99.00 per cent. The first mentioned is for special purposes, the second for casting alloys and structural uses, and the third for deoxidizing.

**Chemical Properties of Magnesium.**—Certain information published on the chemical and physical properties of magnesium is unreliable, since it has been based on determinations and observations made on metal containing appreciable amounts of impurities. The impurities in magnesium may be divided into two classes, *viz.*, metallic and non-metallic. The former include aluminum, barium, calcium, copper, iron, silicon, sodium, and potassium. The non-metallic impurities are usually salts of magnesium such as the oxide and chloride, and chlorides of calcium, potassium, and sodium, as well as occluded bath material and carbon. The bulk of the non-metallic impurities may be eliminated from the reduction-cell metal by a remelting operation.

Pure magnesium (99.99 + per cent) is a silvery-white metal. It consists of three isotopes of masses 24, 25, and 26, in the relative amounts of 7:1:1, yielding a mean atomic weight of 24.336, as compared with the chemical value of 24.32. Magnesium is a basic element and forms salts with mineral and many organic acids. The metal does not oxidize in dry air, but when exposed to moist air it loses its silvery luster

<sup>1</sup> One of the problems of this process is to produce a pure magnesium oxide, since the electrolyte will be contaminated by the progressive building up of any impurities in the added MgO. C. E. Dolbear claims a cyclic process for the production of the pure oxide, based on: (1) boiling impure magnesium oxide with ammonium sulphate, the magnesium going into solution; (2) passing the liberated ammonia into cold pure magnesium sulphate solution.



The reaction is said to be applicable to magnesium carbonate also

and becomes coated with a film of the oxide and possibly carbonate (and hydrate). Magnesium reduces most oxides, liberating the corresponding metal or non-metal. Magnesium has high heat of combustion, the heat of formation of magnesium oxide ( $\text{MgO}$ ) being about 146,000 cal. per gram-atom. The molecular heat of formation of  $\text{Al}_2\text{O}_3$  is about 386,000 cal., or about 128,700 cal. per gram-atom. The explosibility of magnesium dust is high, being about 114 as compared with 100 for standard Pittsburgh coal dust. The metal (particularly in powder or ribbon form) burns easily in air and with an intense white light, very rich in actinic rays. This property makes magnesium valuable in photographic work for flashlights. The spectrum of burning magnesium more nearly resembles that of the sun than any other element. Magnesium does not burn directly in the air to oxide, but is converted first to the nitride, which then burns to the oxide. The reaction is accompanied by a faint yellow glow, followed by the peculiar incandescence and white light. Massive magnesium does not readily burn in air except at temperatures far above the melting point.

Dilute acids dissolve the metal rapidly, with violent evolution of hydrogen. Caustic alkali solutions have no action, but hot aqueous solutions of ammonium salts attack it. Strong sulphuric acid acts slowly on magnesium, and mixed acid (sulphuric plus nitric) has slow action at the ordinary temperature. At  $20^\circ\text{C}$ . water does not attack the metal, but at  $100^\circ\text{C}$ . water is slowly decomposed with the formation of magnesium oxide and hydrogen. The action on hot water is thought to be due to galvanic action between the metal and the impurity iron therein. Magnesium unites with nitrogen below the melting point to form magnesium nitride ( $\text{Mg}_3\text{N}_2$ ) and phosphorus reacts with it to form the phosphide ( $\text{Mg}_3\text{P}_2$ ). With boron it forms the boride, ( $\text{Mg}_3\text{B}_2$ ), and it reacts with carbon to form the carbides ( $\text{MgC}_2$  and  $\text{Mg}_2\text{C}_3$ ). The metal reacts with hydrocarbon gases to form these carbides, setting free hydrogen. It does not react with hydrogen but can be distilled in an atmosphere of this gas. In general, magnesium resists the attack of alkalis and hydrofluoric acid, but is attacked by saline solutions and most acids. The chemical reactions of the metal with numerous substances are given in the handbook of the American Magnesium Corporation.<sup>30</sup>

**Corrosion.**—The information given above as to the action of chemical reagents on magnesium is suggestive in determining the corrodibility of the metal and its alloys. Magnesium and its alloys are more corrodible than aluminum and aluminum alloys when exposed to the ordinary corrosive agents. Some brands of magnesium containing as little as 96 per cent Mg have been placed on the market, and these brands have been high in occluded bath salts. Such salts caused autocorrosion of the metal and gave magnesium the reputation of being unstable. Substantially pure magnesium and light alloys made from such metal exhibit adequate corrosion resistance to ordinary air; they are attacked by solutions of acid salts, neutral solutions of acid salts, and especially by halogen salts. Gasoline, kerosene, and lubricating oils have no action. Solutions of cellulose esters dissolve the metal. Both the metal and its alloys can be protected from ordinary atmospheric and other mild corrosives by painting with lacquers, varnishes, and paints, and by special coatings. Thus, treatment in a bath of sodium bichromate, copper nitrate, and nitric acid causes formation of a colored oxidized layer, probably some copper compound, that protects against atmospheric corrosion. Backer<sup>1</sup> has patented a coating process in which a strongly adherent coating of magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ) is put on by heating the metal or its alloys in

<sup>1</sup> British Patent 173742, Dec. 7, 1921.

water or steam to temperatures above 100°C. for 15 min. under ordinary or raised pressures. The corrosion of magnesium by water can be inhibited by the presence of a small percentage of potassium dichromate in the water.

**Physical and Mechanical Properties of Magnesium.**—Magnesium is the lightest metal used for structural purposes, having specific gravity of 1.74. The

TABLE 3.—PHYSICAL, MECHANICAL, AND OTHER PROPERTIES OF MAGNESIUM<sup>1</sup>

Property	Units for expression	Value
Specific gravity, 20°C .....	Grams per cubic centimeter	1.7388
Specific gravity, liquid, 673°C ..	Grams per cubic centimeter	1.562
Melting point.....	Degrees Centigrade	651
Boiling point.....	Degrees Centigrade	1120
Thermal expansivity.....	Increase in length per unit of length per degree Centigrade (0 to 100°C.)	0.0000259
Thermal conductivity.....	Gram-calories per centimeter cube per degree centigrade per second (c. g. s. units).	0.350
Latent heat of fusion.....	Gram-calories per gram	70
Latent heat of vaporization.....	Gram-calories per gram	1,700
Specific heat .....	Gram-calories per degree Centigrade (20 to 100°C.)	0.249
Specific electrical resistance.....	Microhms per centimeter cubed, at 20°C.	4.46
Temperature coefficient of resistivity.....	Per degree Centigrade (20°C.)	0.0040
Magnetic susceptibility.....	H × 10 <sup>6</sup> , at 18°C.	+0.55
Hardness (cast) .....	Brinell (10 mm., 500 kg., 30 sec.)	30
Hardness (cast) .....	Scleroscope:	
	Magnifier hammer	20.
	Universal hammer	12
Tensile strength (cast) ..	Pounds per square inch	13,000.
Yield point (cast) ..	Pounds per square inch	3,000
Elongation (cast).....	Per cent	6
Reduction in area (cast).....	Per cent	6
Compressive strength (cast) .....	Pounds per square inch	32,000
Transverse strength (cast).....	Pounds per square inch	32,000
Heat of combustion to MgO.....	Calories per gram-atom	146,000
Heat of chlorination to MgCl <sub>2</sub> .....	Calories per gram-molecule	152,000
Heat of sulphuration to MgS.....	Calories per gram-atom	80,000
Electrolytic solution potential against calomel electrode.....	Volts	2.82
Atomic weight.....	O = 16	24.32

<sup>1</sup> Data collected from various sources

metal weighs 109 lb. per cubic foot. The specific gravity in the liquid state (at 673°C.) is 1.56, and the solidification shrinkage is 4.2 per cent. The low value 1.74 for the specific gravity makes an equal volume of magnesium weigh about

two-thirds as much as aluminum. Magnesium is slightly malleable when cold but very malleable and ductile at 350 to 450°C. The metal and certain alloys can be cast readily in iron molds and dry-sand molds and also worked into shapes. Both magnesium and its light alloys machine easily and take a fine finish. When heated *in vacuo*, magnesium sublimates and deposits in crystals. It gives off gas on heating, principally hydrogen and carbon monoxide. Table 3 gives a summary of the physical and mechanical properties of magnesium; the figures may be compared with the corresponding properties for aluminum in the chapter on the Metallurgy of Aluminum and Aluminum Alloys in this work. Magnesium is a good bearing metal. The mechanical properties of some magnesium alloys are discussed below under alloys. Magnesium has low proportional limit and ductility, which features preclude its use for some purposes. Moore<sup>39</sup> gives some recent tests on the mechanical properties of the metal and one alloy.

**Magnesium Alloys.**—Magnesium-rich alloys are the lightest known useful alloys for engineering construction, their specific gravity falling in the range 1.75 to 1.90, roughly. Their tensile strength lies in the range 20,000 to 50,000 lb. per square inch, depending upon the alloy and the condition, *i.e.*, whether cast or worked. Magnesium forms alloys with most metals, and the commercial alloys are represented by certain magnesium-zinc, magnesium-aluminum, magnesium-cadmium, magnesium-aluminum-zinc, magnesium-aluminum-cadmium-copper, and other alloys.

So far, standard specifications for light magnesium alloys have not been drawn and the alloys employed for engineering purposes have been trade alloys principally.

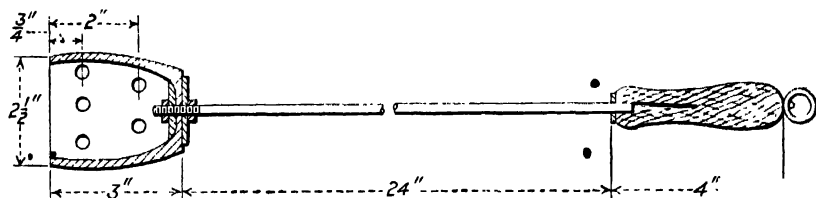


FIG. 4.—Perforated crucible for adding magnesium to alloys. (Rosenhain.)

Thus, magnesium-zinc alloys are represented by the so-called "Elektron metal" of the Chemische Fabrik Griesheim-Elektron, while magnesium-aluminum alloys are made by the Dow Chemical Co. under the name "Dow metal." Substantially pure magnesium and an alloy of the nominal composition 99.5:0.5 magnesium-zinc have been marketed under the name "cork metal." The composition of the trade alloys is variable, so that the trade names cannot be taken to connote anything metallurgically. Light magnesium alloys, largely "Elektron metal," are now used commercially for engineering construction in cast and worked forms, and these alloys are of especial interest to the engineering trades because of their low specific gravity, moderate strength, and high specific tenacity. Magnesium is also a constituent of certain aluminum alloys (*cf.* below). At the present time, magnesium-rich alloys of any kind cannot compete with aluminum alloys until the price of magnesium is less than 50 cts. per pound.

Magnesium-aluminum alloys have been experimented with considerably. These alloys usually contain more than 90 per cent magnesium and less than 10 per cent

aluminum, and the alloy that has been employed considerably commercially has the nominal composition 92:8 magnesium-aluminum. Table 4 gives some figures for the properties of this alloy. According to Gann,<sup>10</sup> the best properties in magnesium-aluminum alloys at the magnesium end are secured in the 96:4 magnesium-aluminum alloy. Data have been published as to the physical properties of "Dow metal D," i.e., the piston alloy (composition not given). These are: tensile strength, 22,000 lb. per square inch; specific gravity, 1.85; specific tenacity, 12,000 lb. per unit weight; impact fatigue (Eden-Foster machine), 190 blows to rupture with 4-in.-lb. blow,

TABLE 4.—MECHANICAL AND OTHER PROPERTIES OF THE 92:8 MAGNESIUM-ALUMINUM ALLOY<sup>1</sup>

Tensile strength:	
Sand castings.....	24,000–25,000 lb. per square inch
Heat treated.....	28,000–30,000 lb. per square inch
Forged.....	45,000–50,000 lb. per square inch
Elastic limit.....	12,000–14,000 lb. per square inch
Elongation on a 2-in. length ..	3–4 per cent
Reduction in area ..	3–4 per cent
Compressive strength.....	43,000–45,000 lb. per square inch
Transverse strength ..	65,000–70,000 lb. per square inch
Shear.....	14,000 lb. per square inch
Tension.....	17,000 lb. per square inch
Modulus of elasticity:	
Tension.....	9,000,000 lb. per square inch
Transverse.....	5,470,000 lb. per square inch
Impact (Charpy) ..	14.66 ft.-lb.
Scleroscope hardness, magnifier hammer ..	22.5
Brinell hardness:	
Sand cast.....	50–55
Forged.....	70
Specific gravity.....	1.79
Electrical resistance ..	14 microhms per centimeter cubed
Thermal conductivity.....	0.295 gm.-cal. per centimeter cubed per degree Centigrade per second
Coefficient of thermal expansion ..	0.000029 per degree Centigrade
Permanent set (upon heating) ..	None

<sup>1</sup> Tests by a magnesium producer

6,000 blows to rupture with 2-in.-lb. blow. Table 5 gives some mechanical properties of a series of magnesium-aluminum alloys in various forms. The commercial magnesium-aluminum alloys sometimes contain small amounts of manganese, silicon, or calcium.

Magnesium-rich magnesium-zinc alloys have been studied considerably in Germany, and some good alloys are secured in the limits of composition up to 10 per cent zinc. The German alloy "Elektron" has the nominal composition 95:5 magnesium-zinc, and, while zinc is the main alloying element used, aluminum, manganese, copper, and cadmium are also frequently present. This alloy is used in the cast or wrought form. Elektron-metal samples have been found to have specific gravity of 1.74 to 1.82, so that evidently substantially pure magnesium has been marketed as Elektron. Some tests have been reported by Beckinsale<sup>15</sup> on the properties of German Elektron metal of the nominal composition 94.5: 5:0.5 magnesium-zinc-copper. The properties of three samples in the form of cylindrical rods were as follows: specific

TABLE 5.—MECHANICAL PROPERTIES OF MAGNESIUM-ALUMINUM ALLOYS

Composition	Density grams per c c	Process of manufacture	Condition or heat treatment	Proportional limit, pounds per square inch	Tensile strength, pounds per square inch	Elongation, in 2 in., per cent	Reduction in area, per cent	Pounds per square inch for $\frac{1}{4}$ per cent extension under load	Compressive strength, pounds per square inch	Shear strength, pounds per square inch	Hardness	
											Brinell hardness, 500 kg. load 10 mm. ball	Shore scleroscope magnifier
96.4 Mg-Al	1.767	Casting (sand)	As cast	2,500	25,000	9	8	7,000	45,000	17,000	42	25
		Extrusion	As extruded	2,500	36,000	20	33	11,000	52,000	19,000	48	28
		Rolling (sheet)	As rolled	2,500	41,000	16.5	19	10,500	52,000	19,000	61	38
		Casting (sand)	As cast	2,000	31,000	15	15	8,500	46,000	19,000	46	32
		Extrusion	Heat treated	2,500	25,000	5	5	6,500	46,000	18,000	46	38
94.6 Mg-Al	1.780	Casting (sand)	As cast	2,000	21,000	17	7	15,000	58,000	22,000	50	35
		Extrusion	As extruded	2,500	41,000	16	21	15,000	58,000	22,000	50	35
		Rolling (sheet)	Heat treated	8,000	41,000	10	10	14,500	58,000	22,000	53	31
		Extrusion	As rolled	5,000	46,000	3	5	11,500	58,000	22,000	75	43
		Rolling (sheet)	Annealed	4,000	38,000	9.5	9	11,500	58,000	22,000	52	30
92.8 Mg-Al	1.790	Casting (sand)	As cast	2,000	20,000	2	2	9,000	45,000	18,000	53	31
		Extrusion	Heat treated	3,000	27,000	5	5	8,500	47,000	20,000	53	31
		Casting (sand)	Heat treated	3,000	30,000	1	1	12,000	53,000	22,000	73	43
		Extrusion	As extruded	10,500	46,000	9	12	15,500	61,000	23,000	59	37
		Rolling (sheet)	Heat treated	8,000	47,000	4	4	15,000	64,000	23,000	68	38
90.10 Mg-Al	1.806	Extrusion	Heat treated	11,000	46,000	7	7	15,000	64,000	23,000	69	40
		Rolling (sheet)	As rolled	5,000	41,000	8.5	8	14,000	58,000	22,000	54	31
		Casting (sand)	Annealed	3,500	19,000	2.5	1	10,000	49,000	19,000	57	33
		Extrusion	As cast	2,500	23,000	2.5	3	9,000	48,000	21,000	55	29
		Casting (sand)	Heat treated	10,000	27,000	8	10	13,000	53,000	25,000	76	43
88.12 Mg-Al	1.820	Extrusion	Heat treated	7,000	47,000	8	10	13,000	66,000	24,000	68	38
		Rolling (sheet)	As rolled	9,000	55,000	2	2	13,000	62,000	24,000	83	50
		Extrusion	Heat treated	4,000	48,000	3.5	5	13,000	62,000	24,000	71	41
		Rolling (sheet)	Annealed	7,000	44,000	3	3	14,500	47,000	21,000	70	40
		Casting (sand)	As cast	4,500	19,000	0.5	None	11,500	47,000	18,000	65	44
		Casting (sand)	Heat treated	15,500	24,000	0.5	1	10,000	49,000	21,000	64	42
		Extrusion	Heat treated	17,500	31,000	0.5	None	16,000	56,000	22,000	94	64
		Rolling (sheet)	Heat treated	12,500	31,000	7.5	8	16,000	62,000	24,000	71	46
		Extrusion	As rolled	13,000	45,000	1	1	16,000	62,000	27,000	90	55
		Rolling (sheet)	Annealed	16,000	53,000	2	2	15,500	62,000	27,000	81	47
		Casting (sand)	As cast	2,500	25,000	9	8	7,000	45,000	17,000	42	25
		Extrusion	As extruded	2,500	36,000	20	33	11,000	52,000	19,000	48	28
		Rolling (sheet)	As rolled	2,500	41,000	16.5	19	10,500	52,000	19,000	61	38
		Casting (sand)	As cast	2,000	31,000	15	15	8,500	46,000	19,000	46	32
		Extrusion	Heat treated	2,500	25,000	5	5	6,500	46,000	18,000	46	38



gravity, 1.78 to 1.79; Brinell hardness (1-mm. ball, 10 kg.), 48 to 63; yield point, 17,000 to 26,900 lb. per square inch; tensile strength, 36,100 to 41,200 lb. per square inch; elongation, 13 to 19 per cent; specific tenacity, 250 to 284; yield point in compression, 6,700 to 18,800 lb. per square inch; and compressive strength, 50,000 to 53,500 lb. per square inch.

The 87:13 magnesium-copper alloy has been employed considerably for pistons in Germany, while the 90:10 magnesium-copper alloy has been used somewhat. The 90:10 magnesium-aluminum, 88:12 magnesium-aluminum, and the 90:8:1:1 magnesium-aluminum-copper-cadmium alloys have all been chill cast for pistons, while the 89:10:1 magnesium-aluminum-silicon alloy has been used for piston-pin bushings. The 87:13 magnesium-copper alloy, sand cast, has tensile strength of about 20,000 lb. per square inch, 1.5 per cent elongation, and 55 Brinell hardness number. Other alloys which have been employed include the 90:5:5 magnesium-aluminum-zinc

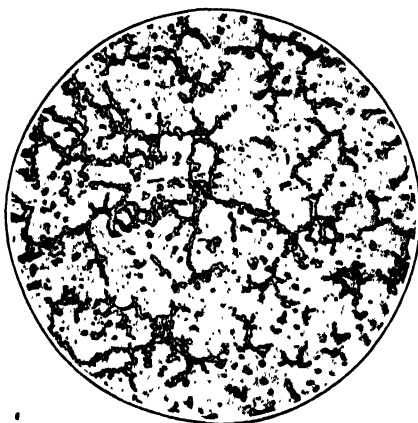


FIG. 5.—Microstructure of 92:8 Mg-Al alloy  $\times 100$ . (Dix.)

alloy (for aircraft castings) and the 99:1 magnesium-silicon alloy (for pistons). Certain of the magnesium-base alloys are heat treatable, *e.g.*, magnesium-aluminum. The heat treatment of such alloys, as in the case of aluminum alloys depends upon the retention in solid solution of a soluble constituent by quenching and its subsequent precipitation in finely dispersed particles by aging. Thus, a heat treatable magnesium-aluminum alloy may be quenched from 425°C. and aged at 200°C. to cause precipitation of the  $Mg_2Al_3$ . Experiments have been carried out on various magnesium alloys, other than those mentioned above, including magnesium-manganese, magnesium-copper-manganese, and magnesium-copper-zinc. A number of compositions have been patented. Certain intermediate alloys, *e.g.*, 50:50 and 20:80 magnesium-copper, have been used for deoxidizing in non-ferrous practice, and the 69:31 aluminum-magnesium alloy has been employed for mirrors under the name mirror metal. Aitchison<sup>27</sup> gives the mechanical properties of several magnesium-base alloys, while Daniels<sup>28</sup> discusses recent developments.

Magnesium is a constituent of certain aluminum alloys, *e.g.*, duralumin, zinc duralumin, magnaliums, and so-called Y-alloy of the National Physical Laboratory (92.5:4:1.5:2 aluminum-copper-magnesium-nickel). Magnesium is present in duralumin and zinc duralumin in amount of 0.5 to 1.0 per cent, and by the formation of magnesium silicide ( $Mg_2Si$ ) is largely responsible for the duralumin phenomenon.

Magnaliums are aluminum-rich alloys containing magnesium alone and up to about 10 per cent or with other elements.

**Melting and Casting.**—Magnesium alloys are more difficult to prepare than aluminum alloys. In practice the magnesium is usually melted in cast-iron or steel pots fired by oil or gas, and the alloys with aluminum and with zinc are made simply by adding definite amounts of the solid metals to liquid magnesium, or the constituent metals for an alloy may be melted and charged together. Burning of the metal on melting is to be avoided, and this can be prevented by exclusion of air or by the use of suitable fluxes. Veazey and Burdick<sup>1</sup> patent a flux for melting consisting of magnesium chloride, barium chloride, and sodium chloride; the metal is floated in a bath of the flux. Gann<sup>2</sup> patents a flux consisting of 42 per cent magnesium chloride, 30 per cent calcium chloride, and 28 per cent sodium chloride, and the method of making this flux. Carnallite has been used as a flux. The salt fluxes prevent burning but have the disadvantage that they become occluded in the metal and in time give rise to auto-corrosion. Schreiber and Beck<sup>3</sup> patent the use of sulphur as a flux; this is placed on the surface. The principle is to cause an atmosphere of sulphur vapor to form above the liquid metal with another layer of sulphur dioxide (formed by combustion with air) above it. Oxidation on melting has been discussed by de Fleury.<sup>4</sup> Magnesium and its alloys have been melted in an atmosphere of hydrogen and *in vacuo*, but this is unnecessary. The melting temperature for the metal and its alloys should not much exceed 720°C.

Magnesium cannot be poured into green-sand (water-tempered) molds, since it will react with the moisture. Sand molds may be baked dry, or for "green"-sand work the usual water is replaced by an inert bond such as kerosene, glycerine and the like, which will prevent ignition of the hot metal. Cores may be bonded with dextrin or sodium silicate solution and baked. Wilhelmy<sup>5</sup> patents the use of sodium silicate as a core binder. The sand for magnesium-alloy castings should be coarse and permeable, and the molds should be rammed lightly and vented freely. In drying molds, heating at 450°C. for 3 hr. is suitable. Magnesium-base alloys can be poured into permanent molds and also die cast with plunger-type machines.

As indicated previously (*cf.* also Uses below), magnesium is used to a considerable extent as a deoxidizer in non-ferrous foundry practice. It is also a minor alloying element or a constituent in subordinate amount in certain alloys. For making fixed additions of magnesium, it is advisable not to add the entire amount at once by simply throwing the metal into a liquid melt, but small pieces may be pushed under the surface by tongs and held until dissolved. If thrown into a liquid melt, the magnesium will break up, float on the surface, and burn. A useful device for making fixed additions of magnesium is a form of "phosphorizer," such as is used in adding phosphorus to alloys. The tubular device patented by Naylor and Hutton<sup>6</sup> is useful, or the perforated crucible<sup>16</sup> shown in Fig. 4 may be employed.

**Mechanical Treatment.**—Both magnesium and certain magnesium-rich alloys can be readily rolled hot and to some extent cold, but when rolled cold frequent annealings are necessary between passes in order to avoid cracking. Both the metal and magnesium-base alloys containing for example up to 10 per cent aluminum or zinc are worked (rolled or forged) at 350 to 400°C., and extruded at 550°C. The ordinary ribbon is made by pressing the semifluid metal into wire and then flattening it. The powder is made by disintegrating the metal in the pasty condition, or by milling. Magnesium and its alloys are soldered with great difficulty, but welding is done similar to aluminum welding. The use of a slightly reducing oxyacetylene flame and fluoride fluxes is recommended. Both magnesium and magnesium alloys may be machined very rapidly and easily, and the machineability of magnesium is unexceeded by any other metal. It exhibits no dragging tendency as does aluminum, and all machine-tool operations can be carried out much faster than on aluminum and its alloys.

**Metallography.**—Magnesium has a hexagonal close-packed lattice, with lattice parameter  $a = 3.22$  and  $c = 5.23$  (axial ratio 1.624). Magnesium does not work well because of its crystal structure. The ductile and malleable metals (like aluminum) have face-centered cubic lattices. The constitution and metallography of many binary systems of magnesium with other metals have been examined, and the diagrams of thermal equilibrium published.<sup>30</sup> Magnesium and its alloys may be etched satisfactorily with dilute acids, *e.g.*, acetic acid and nitric acid. A solution of 1 per cent hydrochloric acid plus 0.5 per cent nitric acid in alcohol is also a satisfactory etching reagent. Figure 5 shows the microstructure of the 92:8 magnesium-aluminum alloy.

**Uses and Applications of Magnesium and Magnesium Alloys.**—As stated, magnesium and its light alloys have so far been employed only slightly in American engineering practice as structural materials, but in Germany they are used in direct competition with aluminum.<sup>1</sup> The principal uses of magnesium may be summarized as follows: (1) as the substantially pure metal for structural purposes; (2) as an alloy for structural purposes, notably in automotive work, aircraft, and in the electrical industry; (3) as a minor constituent of alloys, principally aluminum-rich alloys; (4) as the substantially pure metal (and also as intermediate alloys) for scavenging and deoxidizing, principally in non-ferrous practice; (5) as the substantially pure metal in powder or ribbon form as an illuminant in photography and for military purposes.

In engineering applications, magnesium can generally be used as a substitute for aluminum and the magnesium alloys for aluminum alloys where a light material is desired. At the present time, cast light magnesium alloys are used considerably in Germany for crank cases, pistons, transmission housings, gear cases, hub caps, and other castings in the automotive industry, for general castings in the electrical industry, for typewriters, and for many other purposes. Wrought alloys, chiefly in extruded form, are used extensively for the construction of cameras, binoculars, and field glasses, machinery parts, and instruments of precision. Both castings and worked parts have been used considerably in the construction of aircraft, and also for certain military equipment, including fuse parts and gun and rifle parts. The German alloy "Elektron" has been used for electrical conductors, principally in bus-bar

<sup>1</sup> Private communication, Sept. 8, 1923.

form. In the United States, the U. S. Army Air Service has used the 96:4 magnesium-aluminum alloy (containing a small amount of manganese) for crank-cases, super-charger casings, instrument covers, camera mounts, etc. Fig. 6 shows a group of magnesium-base alloy castings for aircraft. While the magnesium-rich alloys are of great interest because of their low specific gravity and high specific tenacity and can be employed in competition with aluminum in Germany at the prices there now ruling, they cannot compete with aluminum alloys in the United States until the price of magnesium is at least 50 cts. per pound. "Dow metal" has been used for pistons, and experimentally for connecting rods, bolts, nuts, and bearings. The uses of magnesium and its alloys have been detailed by Flusin.<sup>14</sup> Magnesium is a minor constituent in certain alloys, notably the duralumin-type alloys and magnaliums.

Magnesium is employed considerably in non-ferrous foundry practice as a deoxidizing agent, being used in the production of brass, bronze, aluminum alloy, copper, nickel alloy, and other castings. In aluminum-alloy foundry practice, it is used with the idea of deoxidizing aluminum-alloy melts, which it does not do, but it does degasify melts and also decreases the grain size. Although the heat of formation of magnesium

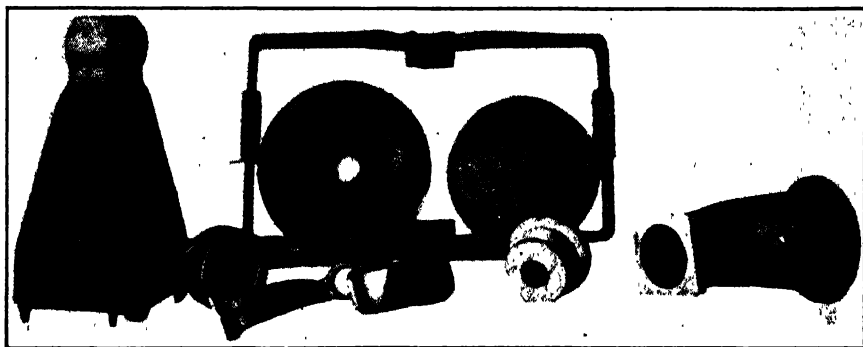


FIG. 6.—Aircraft castings in magnesium-base alloys. (Danicls.)

oxide is generally given as greater than that of aluminum oxide (gram-atom basis), the heats of formation are doubtless quite close together. Biltz and Hohorst give the heats of formation as 113,110 cal. for magnesium oxide and 125,100 cal. for aluminum oxide. Magnesium will reduce carbon monoxide and dioxide at the temperature of liquid aluminum and hence is useful as a degasifier. For aluminum-alloy work, about 0.5 per cent magnesium is added.

For deoxidizing, either the pure metal or an intermediate alloy, such as magnesium-copper, magnesium-silicon, or magnesium-aluminum, may be used. When employed for deoxidizing casting copper, about 0.03 to 0.08 per cent is added, and for brass and bronze about 0.1 per cent is used. Magnesium is essential as a deoxidizer in nickel metallurgy, being used to deoxidize nickel ingots for rolling and monel metal for casting; 0.08 to 0.15 per cent magnesium is added. Pure nickel is actually malleable but is rendered non-malleable by the presence of so little as 0.005 per cent sulphur. Magnesium forms  $MgS$  (probably) with the sulphur, and this compound does not affect the intercrystalline cohesion. Recent tests indicate that magnesium additions have a deleterious effect on the tensile properties of brass castings. An uranium-magnesium-aluminum alloy has been employed as a deoxidizer in steel practice, particularly for chrome steels. In general, magnesium is a useful dioxidizer for scavenging metals and alloys, thereby cleaning up occluded oxides, causing degasification, and yielding denser and stronger castings.



## CHAPTER XXI

### THE ALKALI AND ALKALINE-EARTH METALS

BY HOWARD E. BATSFORD<sup>1</sup>

**The alkali metals** usually met with are potassium, sodium, caesium, rubidium, and lithium. The radical  $\text{NH}_4$  resembles these metals in its properties, and chemically is classed with them.

The metals of this group decompose water at ordinary temperatures with the evolution of hydrogen and the formation of strongly alkaline-reacting hydroxides, which cannot be freed from their hydrate water even on fusion. The pure oxides ( $\text{R}_2\text{O}$ ) are difficult to prepare, even cautious heating of the metal in air forming peroxides at the same time. The salts of these metals are colorless for the most part, and readily soluble in water. Of these salts the carbonates, the tertiary and secondary phosphates, the cyanides, and the borates react alkaline in aqueous solution (hydrolysis). The salts of the alkalis are more or less volatile and impart to the non-luminous flame characteristic colors.

**Potassium** (K—atomic weight, 39.15; specific gravity, 0.87; melting point,  $62.5^\circ\text{C}$ .; boiling point,  $667^\circ\text{C}$ .).—Potassium is the lightest metal known, with the exception of lithium. It is a silvery-white metal tinged with blue. It is oxidized on exposure to air, forming a film of oxide, and on prolonged exposure deliquesces into a solution of hydrate and carbonate. Perfectly dry oxygen does not affect it. It is soft at ordinary temperatures and can be kneaded between the fingers or cut with a blunt knife. An intensely green vapor is given off on boiling, and it crystallizes in quadratic octahedra of greenish-blue color. Heated in air, it fuses and takes fire; when thrown in small pieces on the surface of water it bursts into a violet flame. At 300 to  $400^\circ\text{C}$ . it occludes hydrogen gas, forming  $\text{K}_2\text{H}$ . Its electrical conductivity at  $50^\circ\text{C}$ . is  $11.6 \times 10^4$  reciprocal ohms; at  $100^\circ\text{C}$ .,  $6.29 \times 10^4$  for liquid. The spectrum is reddish. The heat of formation of KOH is 101.7 to 103.17 cal.

**Occurrence.**—Potassium occurs in nature in the minerals sylvite ( $\text{KCl}$ ), and carnallite ( $\text{Mg Cl}_2 \text{KCl} \cdot 6\text{H}_2\text{O}$ ) at Stassfurt in the presence of halite and anhydrite. A common form is saltpeter ( $\text{KNO}_3$ ) in orthorhombic prisms, and in many silicates, as monoclinic feldspar ( $\text{KAlSi}_3\text{O}_8$ ) and muscovite ( $\text{KH}_2\text{AlSi}_3\text{O}_{12}$ ). Two other sources of potassium are the organic salts of plants which on burning yield potassium carbonate (potash) and the dust from the burning of cement, which on leaching furnishes much potash.

Inland deposits of the salt ( $\text{KCl}$ ) at Salduro, Utah, and Searles Lake, are the base of large-scale operations. At these places the salt is harvested with large plows, conveyed to the plant where the potash salt is leached, and concentrated in pure or commercial form. The ratio of soda to potash in ocean water is 100 to 3.23; in kelp it is, on the average, 100 to 5.26.

<sup>1</sup> Chemical engineer, Utica, N. Y.

**Metallurgy.** (1) *Chemical*.—The metal has been obtained by passing melted potash down a clay tube containing iron turnings or wire heated to whiteness; also by the use of charcoal at white heat. Brunner's process consisted in forming an intimate mixture of potassium carbonate and carbon by igniting crude tartar in a covered iron crucible, cooling the mass, then distilling it at a white heat from iron bottles, the vaporized metal being condensed beneath the surface of paraffin or naphtha contained in a copper vessel. The metal is purified by redistilling and condensing directly under paraffin.

2. *Electrochemical Methods*.—Linnemann electrolyzes the cyanide (KCN) between carbon electrodes. A. Matthiessen electrolyzes an equimolecular mixture of potassium and calcium chlorides (melting at a lower temperature than potassium chloride) between carbon electrodes. Castner electrolyzes caustic potash in fused state with nickel anode and iron cathode.

**Important Uses.**—Potassium combines with chlorine and bromine with great energy, and has the power to extract chlorine from its compounds. It can, therefore, be used for isolating some compounds, as, for example, magnesium and aluminum, whose oxygen compounds cannot be reduced by the ordinary methods. Sodium, however, can be obtained at a lower price and is used instead. An alloy of sodium and potassium which is liquid at ordinary temperatures is used as indicator in thermometry.

**Chief Alloys and Compounds.**—*Potassium Hydride* ( $K_2H$ ).—This compound, formed by heating potassium in an atmosphere of hydrogen at about  $300^\circ C.$ , is a silvery-white mass with a metallic luster. It takes fire in air and when heated begins to dissociate at  $200^\circ C.$

*Potassium Bromate* ( $KBrO_3$ ).—A crystalline powder, sometimes needles, soluble in hot water, slightly soluble in alcohol. It melts at  $350^\circ C.$ , and decomposes first slowly and then rapidly and explosively, giving off  $O_2$  and  $Br_2$ .

*Potassium Chlorate* ( $KClO_3$ ).—Transparent, colorless shining prisms or monoclinic plates, with pearly luster and cooling saline taste. It is a good oxidizing agent; decomposes with evolution of  $O_2$ , when heated to  $352^\circ C.$ ; is decomposed by strong acids, often with explosive violence; is soluble in water, with absorption of heat; soluble in alcohol, but insoluble in absolute alcohol; melting point,  $334^\circ C.$

*Potassium Chloride* ( $KCl$ ).—White cubical crystals with saline taste, stable in air; decrepitates when heated; soluble in water and alcohol, insoluble in absolute alcohol, and very slightly soluble in ether-absolute alcohol. Melting point,  $730^\circ C.$ , and volatile at higher temperatures. It is used as a source of potassium hydroxide in the Nelson and Allen-Moore cells.

*Potassium Chromate* ( $K_2CrO_4$ ).—Pale, lemon-yellow, chunky, double, six-sided, trimetric pyramids, with alkaline reaction and bitter, cooling, metallic taste. It melts without change at red heat, is easily soluble in water, insoluble in alcohol, and is one of the most common oxidizing agents.

*Potassium Bichromate* ( $K_2Cr_2O_7$ ).—Large, orange-red, translucent, four-sided, triclinic plates or prisms, stable in air, with acid reaction and bitter metallic taste. It decrepitates when heated, melts near red heat, and decomposes at red heat. Less soluble in water than  $K_2CrO_4$ , and insoluble in alcohol.

*Potassium Ferricyanide* ( $K_3Fe(CN)_6$ ).—Large, red, monoclinic prisms, or needles, which when crushed give a yellow powder; easily soluble in water to a greenish solution, insoluble in absolute alcohol, and slightly soluble in dilute alcohol.

*Potassium Ferrocyanide* ( $K_4Fe(CN)_6 \cdot 3H_2O$ ).—Lemon-yellow to amber-yellow, efflorescent, monoclinic, tabular crystals, seldom separate, usually massed together

irregularly. Pearly luster as crystals, but loses all its water of crystallization at 60 to 80°C. Decomposes when heated to a higher temperature. Soluble in water to a yellow solution that decomposes in sunlight with formation of Prussian blue. More soluble in hot than in cold water, and insoluble in alcohol.

*Potassium Manganate* ( $K_2MnO_4$ ).—Dark-green rhombic crystals, with metallic luster, turning dull and black in air. Decomposes when heated to a high temperature, soluble in water, with decomposition to  $KMnO_4$  and  $MnO_2$ , soluble in  $KOH.Aq.$ , from which it may be crystallized.

*Potassium Permanganate* ( $KMnO_4$ ).—Dark, purple-red, almost black, slender, opaque prisms, with blue metallic reflection, sweet taste, with astringent bitter after-taste. Decomposes at high heat, is soluble in water, giving an aqueous solution violet to purple when dilute; dark red to nearly black when concentrated; is decomposed immediately by alcohol.

*Potassium Nitrate* ( $KNO_3$ ).—Colorless, transparent, six-sided prisms or a white, crystalline powder with cooling saline, pungent taste. Soluble in water, with lowering of temperature, insoluble in absolute alcohol, but in dilute alcohol it dissolves proportionally to the amount of water present. Decomposes at white heat. Melting point, 339°C.

*Potassium Nitrite* ( $KNO_2$ ).—White to yellowish-white, amorphous, deliquescent sticks or lumps, resembling  $KOH$ , or colorless microscopic, prismatic crystals; very soluble in water—more so than  $KNO_3$ —insoluble in absolute alcohol. Forms an insoluble double salt  $(CO(NO_2)_2)_3 \cdot 3KNO_2$  with  $Co$  nitrite.

*Potassium Oxide* ( $K_2O$ ).—Grayish-white, brittle, non-lustrous solid with conchoidal fracture, often contaminated with  $K_2O_2$ , soluble in water, with evolution of much heat and formation of  $KOH$ . Melts at full red heat, volatilizes at very high temperatures.

*Potassium Persulphate* ( $K_2S_2O_8$ ).—White crystals, slightly soluble in water. It is used for bleaching and is an exceedingly powerful oxidizer and antiseptic.

*Potassium Sulphocyanate* ( $KSCN$ ).—Long, white striated prisms resembling niter, sometimes colorless scales. Very soluble in water, with lowering of temperature; soluble in alcohol. Melts at 161°C, the fluid salt turning brown at first, then green, finally indigo blue, but returning to a white solid on cooling.

*Potassium Tungstate* ( $K_2WO_4$ ).—White, deliquescent, triglinic needles, decrepitate when heated, melts at red heat, easily soluble in water, insoluble in alcohol. It is used in manufacture of magenta bronze.

**Sodium** ( $Na$ —atomic weight, 22.82; specific gravity, 0.9735; melting point, 95.6°C., boiling point, 742°C).—It is a light, soft, malleable, ductile metal, occasionally forming lustrous white, quadratic octahedra, silver-white and very lustrous when freshly cut, but oxidizes easily on exposure to air, becoming dull gray. Evolves hydrogen rapidly from cold water, leaving  $NaOH$  in solution, and the hydrogen generally does not catch fire. Burns in air with a yellow flame, the oxide formed being a mixture of  $Na_2O$  and  $Na_2O_2$ . Must be kept in air-tight cans or under a liquid, free from oxygen, such as naphtha. Fairly hard at  $-20^\circ C.$ , ductile at  $0^\circ C.$ , soft as wax at ordinary temperature, pasty at about  $50^\circ C.$ , melts about  $95^\circ C.$ , and boils at about  $750^\circ C.$  Vapor is colorless or violet. Soluble in liquid ammonia; decomposes alcohol violently; insoluble in hydrocarbons; reacts violently with acids, forming soluble salts. The metal may be heated to melting or even higher temperature without catching fire. Combines with the halogens when heated. All  $Na$  salts color the bunsen flame yellow.



Electrical conductivity at 21.7°C.,  $22.4 \times 10^4$  reciprocal ohms or 36.5 per cent of value of Ag.

Electrical conductivity at 50°C., solid Na  $18.8 \times 10^4$  reciprocal ohms.

Electrical conductivity at 116°C., solid Na  $9.8 \times 10^4$  reciprocal ohms.

Electrical conductivity at 120°C., liquid Na  $11.42 \times 10^4$  reciprocal ohms.

Heat of formation of NaOH, 101.87 to 102.7 cal. •

It ranks fourth to silver, copper, and gold in electrical conductivity and heat conductivity and is the most electropositive metal with the exception of caesium, rubidium, and potassium.

**Occurrence.**—Sodium occurs in nature very extensively. Its most important mineral, of course, is halite, or rock salt ( $\text{NaCl}$ ), isometric system. It is found in very large deposits, often quite pure, but usually contaminated with clay, anhydrite, and gypsum, and is present in large amounts in the ocean and in many salt springs.

Sodium also occurs in the form of carbonate, as thermonatrite ( $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ), natrite or soda ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ), trona ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ), as nitrate in Chile saltpeter ( $\text{NaNO}_3$ ), as cryolite ( $\text{Na}_3\text{AlF}_6$ ), in many silicates as albite ( $\text{NaAlSi}_3\text{O}_8$ ), and as tinkal, borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ).

**Metallurgy.** (1) *Chemical.*—The chemical production of metallic sodium consisted largely of methods for the reduction of the chloride and the carbonate.

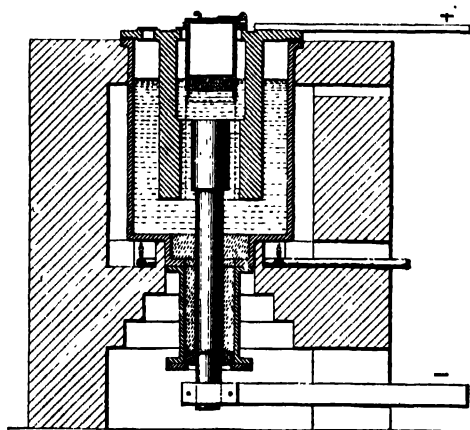


FIG. 1.—Castner cell.

For the reducing agent carbon in various forms has been used. Gay-Lussac and Thenard decomposed sodium hydroxide with red-hot iron; Brunner ignited sodium carbonate with charcoal; Netto heated a column of coke or charcoal in a retort or receiver to a high temperature, then sprayed fused NaOH on the red-hot mass. Decomposition took place rapidly and the vapors of sodium escaped through the spaces between the charcoal. In 1903 T. Parker mixed aluminate of soda with carbon in suitable proportions and calcined them in an electric furnace. Sodium distilled off and alumina was left. The work of Freeman in 1919 differed from others in that he used salt and calcium carbide in finely powdered condition and heated them to a bright red temperature, not higher than 1400°C.<sup>1</sup>

<sup>1</sup> U. S. Patent 1319148.

2. *Electrochemical*.—The difficulties to be contended with in the electrochemical manufacture of metallic sodium from fused salts are the destructive action of fused chlorides and the reduced alkali metals on most non-metallic substances available for the containing vessel and its diaphragm, also that of the anode chlorine on metals. The low fusion point of metallic sodium ( $95^{\circ}\text{C}.$ ) and of potassium, ( $62^{\circ}\text{C}.$ ) and the low specific gravity of the metals cause the separated metals to float on the surface of the melted salt. Again, pure sodium chloride melts at about  $775^{\circ}\text{C}.$ , while sodium boils at  $750^{\circ}\text{C}.$ , so that the margin of safety is very small if loss by evaporation is to be prevented.

Electrolysis of fused caustic soda with a nickel anode and iron cathode and the use of an iron-wire gauze diaphragm is attributed to Hamilton Y. Castner, and is in successful operation at the present time. Oxygen is evolved at the anode and escapes from the outer vessel, while the sodium is deposited in globules on the cathode surface. It then frees itself and floats upwards into the iron cylinder, within which it accumulates and from which it may be removed at intervals by means of a perforated iron ladle.

Owing to the surface tension of the sodium it remains in the ladle while the fused salt passes freely through the perforations. The sodium is then cast into

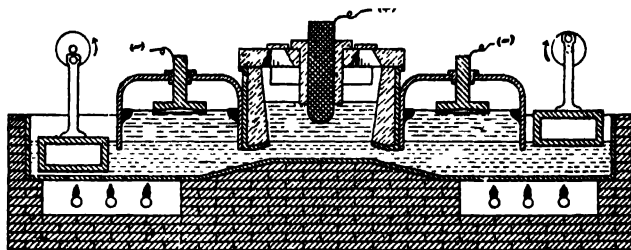


FIG. 2.—Carrier fused-salt cell.

molds for use in the arts.  $\text{NaOH}$  has certain advantages over  $\text{NaCl}$ , although it is more costly. Its fusing point is only  $320^{\circ}\text{C}.$ , and no anode chlorine is produced, so that both containing vessel and anode may be of iron, and no porous partition is necessary.

C. F. Carrier in 1906 patented a cell in which he electrolyzed fused salt. (See Fig. 2, taken from U. S. Pat. 830051; Sept. 4, 1906.) For this purpose he had the anode compartment equipped with graphite anodes and the cathode compartment, which was on the other side of a division wall, equipped with a flat iron plate for cathode. The intermediate electrode was molten lead, which was caused to flow back and forth by the action of two heavy plungers.

The melt in the cathode chamber was fused caustic soda kept just a little above its melting point. The cell was started by piling a little salt around the anode, which was lowered almost to the lead (the latter being in molten condition). When an arc had been formed between graphite and lead, some of the salt melted from the intense heat, and by gradually drawing the anode away from the lead and feeding in salt the bath was built up. Care had to be exercised at this time not to pass the current through the cathode, otherwise the lead would be attacked due to the absence of sodium. When, however, the bath was partly built up, the current was put through the regular channels.

The sodium was deposited in the lead, which conveyed it to the cathode compartment, there to be set free at the iron cathode and collected under paraffine after its exit from the overflow pipe.

To prevent shorting of the current from cathode to bell-covering compartment, a water-cooling pipe was placed on the inner edge of the bell-shaped top of the cathode compartment. This permitted the bath to be kept in solid condition, and hence a good insulator.

One of the chief difficulties which seems apparent in this type of furnace is the control of temperature in the furnace. In spite of the inventor's claims to regulation by means of the water cooling, there still remains the fact that the temperature must drop from about 800 to 300°C. in the space of a few inches. It has also been found that the iron castings do not hold lead tightly and are subject to deterioration, hence it seems like placing too many eggs in one basket.

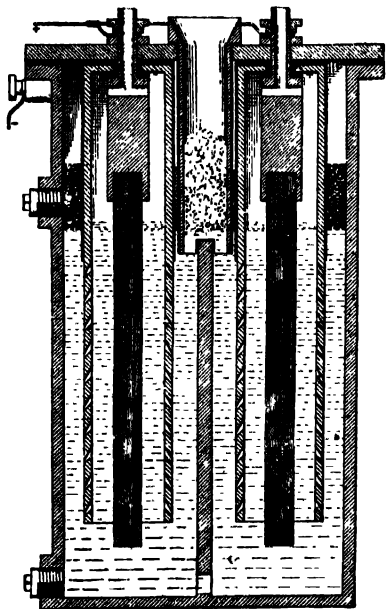


FIG. 3. --Darling cell using sodium nitrate.

J. D. Darling had meanwhile invented a process for making metallic sodium from sodium nitrate, carrying on the experimental work at the Philadelphia plant of Harrison Bros. & Co., Inc. Fig. 3 represents the cell as described in U. S. Pat. 517001; March 20, 1894.

For anodes he used carbon-platinum rods set in compartments with perforated inverted bell of aluminum enveloping them. This bell was fitted with perforations sloping down from the inside to prevent the outward flow of the gases generated during electrolysis. The iron pot served as cathode, air being excluded by a tight cover. Sodium nitrate was melted in the pot, the top cover and electrodes were set in place, and the current was turned on. The molten nitrate was reduced to nitrite of soda with the addition of sodium oxide, the latter dissolving in the nitrite of soda. The nitrite of soda and the sodium oxide were then decomposed, permitting the liberated sodium to float to the top of the bath and pass down through a suitable outlet pipe. Gaseous  $\text{NO}_2$  and  $\text{O}_2$  passed off through an opening in the top of the anode chamber and were led through

absorption bottles containing water, thus forming nitric acid and permitting the oxygen to escape.

He later invented a porous diaphragm of portland cement and improved his cell, and attempted to market his process. Unfortunately the explosion hazard was too great a drawback, and the process was abandoned about the year 1905.

Electrolysis of fused salt mixtures, such as sodium chloride and calcium chloride; sodium chloride, calcium chloride, potassium chloride, and barium chloride were used by Seward and von Kugelgen and also by McNitt. Seward electrolyzed mixtures of anhydrous salts of  $\text{NaCl}$ ,  $\text{KCl}$ , and the fluorides, endeavoring to get mixtures of low fusing point. His furnace consisted of a large shallow pot lined with special heat-resisting brick in which was embedded the graphite anode ring. The cathode consisted of a hollow iron cylinder made up of a double shell united at the top and filled with asbestos, built into the furnace body, the current leaving through the bottom. This cathode was covered by a hood dipping just beneath the surface of the molten mixture to prevent admission of air to the molten sodium which rose to the top of the cathode, flowed across to a center hole, and thence to a receiver fastened to the lower

end of the cathode. As the electrodes were a considerable distance apart, there was no need of a diaphragm to separate the anions from the cations.

The insulation of the cathode was effected by causing a frozen layer of salt to be maintained at the junction of the cathode with the furnace bottom. The large distance between anode and cathode caused the voltage to be higher than in the furnaces described later. A layer of frozen salt was maintained around the edge of the diaphragm by means of a water-cooling coil placed in its edge.

McNitt's furnace depended on a deep layer of molten salts above the zone of electrolysis to keep the sodium in the condensed form for collecting. The furnace was built in the shape of a circular well with graphite anodes set in a ring near the bottom. The cathode was of the hanging type, being supported from a tripod independent of the furnace body. It consisted of a steel cylinder on the end of a suitably insulated conductor, carried a well-insulated hood and wire-gauze diaphragm and was further protected from damage by a water cooler inserted in the center of the conductor for almost the entire length of the electrode.

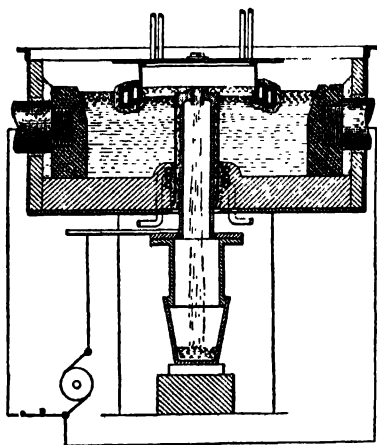


FIG. 4.—Seward and von Kugelgen's fused salt cell

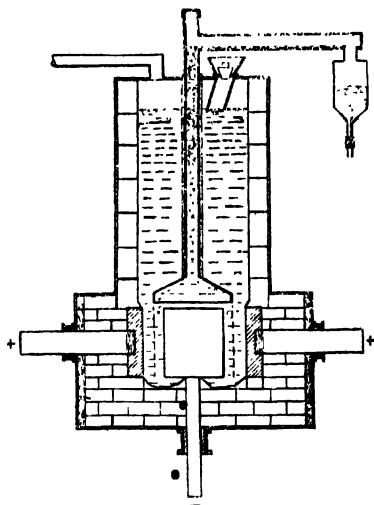


FIG. 5.—McNitt cell.

All radiation possible was saved by protecting the outer surface of the furnace with layers of kieselguhr or Sil-O-Cel fire brick and the graphite anodes had water coolers on the outer ends of the stems. Sodium metal rose from the cathode surface into the hood, ascended through a vertical outlet pipe, and flowed across into a receiver outside the furnace and was kept warm by a resistance coil or gas flame surrounding it.

The chlorine gas in all types of furnace is drawn from the space above the bath through a suitably placed pipe in the furnace wall.

Many types of furnace have been devised, such as one in which the anode is surrounded by a hollow cathode, necessitating the removal of the sodium from the outside of the furnace and carriage of the chlorine from the center. These types are still in the experimental stage and depend a great deal on the manner of heat insulation and anticorrosion protection.

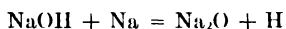
Borchers made a study of the production of metallic sodium and arrived at the following conclusions in 1894: For best electrolysis: (1) Alkali metal must be deposited

at a metallic (iron) cathode. (2) Cathode space must permit of collection and removal of metal without the latter coming in contact with reducible substances. (3) The anode must be of carbon. (4) The anode space must permit of the easy removal of the halogen, and its walls must be constructed of material capable of withstanding the action of halogens and haloid salts. (5) No metallic particles should be present in the melt between the poles. (6) All the parts of the apparatus must be constructed of fire-resisting material.

In 1902 Janeczke made a special study of the decomposition voltages occurring in the electrolysis of fused caustic soda.

At temperatures corresponding to the melting point of caustic soda, the sodium is absorbed during electrolysis, as is also oxygen; at slightly higher temperatures these products are absorbed so rapidly that there is no decomposition.

Hydrogen may be formed primarily by deposition at the cathode or secondarily by action through the sodium and water formed at the anode, the following reaction taking place:



Therefore there are present H ions in small number in the fused anhydrous caustic soda.

The decomposition voltage was found to be about 1.3 volts for caustic soda. Below 1.0 volt at the cathode a quite lively generation of hydrogen takes place, the oxygen generation taking place promptly at 1.3 volts.

The second decomposition point in the voltage curve is at 2.1 volts. At 2.4 volts stream lines seemed to go out from the cathode into the melt with flashes of gas. These were apparently sodium particles which reacted with the caustic soda.

From these and other data it was assumed that 2.2 volts represents the point at which metallic sodium is formed.

Le Blanc and Brode published in the same year (1902) in *Zeitschrift für Elektrochemie* the results of their observations on the electrolysis of fused NaOH and KOH, as follows:

At the anode oxygen and water are formed, the water reacting with the sodium freed at the cathode with the evolution of hydrogen.

Since one equivalent of water exists for two equivalents of sodium, a current yield of 50 per cent is the maximum obtainable in such a process as that patented by Castner. In fact, the yield generally runs about 40 per cent.

At high temperatures sodium dissolves in the melt, causing evidently strongly depolarizing properties in the melt at the anode. The depolarizing effect of the dissolved sodium was so great that only at high current densities could oxygen be formed. Under these conditions the gas formed at the anode was a mixture of equal parts of hydrogen and oxygen, or detonating gas mixed with hydrogen. Sometimes the cell works badly, makes little sodium, and almost every minute has an explosion. It is then too hot, the melt is dissolving too much sodium, it partly depolarizes the anode, and partly reacts with the moisture present, forming rich mixtures of detonating gas which explode.

At a lower temperature, on account of the diminished solubility of the sodium in the melt, the depolarizing effect at the anode and the formation of detonating gas are reduced to a minimum.

The Castner process furnishes a means for conducting the hydrogen upwards inside a wire gauze along with the metallic sodium, neither being permitted to pass across to the anode.

The anodic gas generation is not, as Castner believed, a result of the increased solubility of oxygen in the melt, but is a result of the depolarizing action of the dissolved sodium. If the former were true, anodic hydrogen would be liberated, whereas free oxygen and the water are formed.

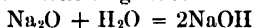
If sodium peroxide is dissolved in the melt, it has the same depolarizing action as the metallic sodium, but at the cathode.

In a pure caustic soda melt there is nothing which exerts a depolarizing action at the anode or cathode, and on this account only small currents pass through the electrolyte at low terminal voltages.

Peroxide exists at the anode and dissolved sodium at the cathode, both of which act as depolarizer for the other electrode. On continued electrolysis, the following reaction takes place:



With water at the anode the following reaction:



A part of the sodium also acts directly on the water. According to the reaction which predominates, the result is a melt saturated with sodium or with sodium peroxide. Luckily, it is possible to get anodic or cathodic polarization at will, if fresh electrolyte is allowed to flow either from anode to cathode, or *vice versa*.

In order to obtain good yields of sodium, the following precautions are in order: (1) Do not let the water formed at the anode reach the cathode; (2) get a good diaphragm.

Pure anhydrous caustic soda contains no H ions nor O ions but only Na and OH ions, and is very hygroscopic.

The Acker process consists in electrolyzing pure sodium chloride in a furnace having graphite anodes and a lead cathode. In a large shallow casting with false bottom several graphite anodes dip for about 1 in. into a fused salt bath, which is resting on a layer of molten lead as cathode. The chlorine gas is drawn from the furnace top by means of an exhaust fan, and the sodium is absorbed by the molten lead, which flows through a subterranean channel to an auxiliary chamber for removal of the sodium by steam. The rejuvenated lead is returned again to the electrolytic chamber for more sodium.

The chlorine gas, containing about 10 per cent  $\text{Cl}_2$  and 90 per cent air, is drawn through lime liquor for the formation of chlorine products.

The current used is 6,000 amp., the voltage 7 volts, and the current density 2.9 amp. per square centimeter.

Hambuechen made a study of the electrolysis of NaOH by alternating current with the following results: The property of aluminum electrodes, which permits the electricity to pass in one direction only, is made use of for electrolyzing caustic soda. NaOH is fused in an aluminum vessel, in which is placed an aluminum electrode surrounded by an iron electrode. A perforated aluminum diaphragm is interposed, insulated from the aluminum electrode by a porcelain sleeve. Alternating currents of 9 amp. at 4 volts gave a good yield of sodium under careful temperature regulation, with very little corrosion of the aluminum.

In 1906 C. F. Carrier published the following figures and facts concerning the Castner process: Advantages: low melting point of bath; simplicity of the apparatus. Disadvantages: high cost of raw materials; low ampere efficiency; small size of the units; constant explosions during process; the metal is removed in dribblets by dipping out with a spoon.

#### COST FIGURES (1906)

Daily production.....	1 ton of Na
Ampere efficiency.....	40 per cent
Fall of potential .....	5 volts per cell
Capacity of cells .....	1,200 amp.
Capitalization.....	\$30,000

360 days per year; 24 hr. per day

## COSTS PER YEAR

650 tons NaOH at \$45.....	\$29,250
725 hp.-yr. at \$20.....	14,500
30 men at \$2 a day per man.....	21,600
Management and expert labor.....	9,000
Interest and depreciation (15 per cent).....	7,500
General expenses and selling, 5 per cent sale price.....	9,000
Miscellaneous supplies.....	1,000
Total.....	\$91,850
Yearly production, 720,000 lb.	
Approximate cost per pound.....	12 7 cts.

In spite of the rapidly decreasing solubility of the sodium and potassium at higher temperatures, the electrochemical efficiencies in electrolysis of NaOH and KOH rapidly decrease with rising temperature as a result of the increase of velocity with which the metal diffuses into the molten electrolyte.

Measurements show this velocity to be greater for sodium than for potassium, and in the former case to increase rapidly above 340°C., at which point the efficiency for NaOH electrolysis sinks nearly to zero.

Le Blanc and Bergmann made a study of the influence of metals on fused hydroxide, which gave an idea to the metallurgist as to what to expect in the construction of cells for this electrolysis.

For the tests they prepared NaOH, which analyzed as follows: NaOH, 92.6 per cent;  $\text{Na}_2\text{CO}_3$ , 4.95 per cent; and  $\text{H}_2\text{O}$ , 2.45 per cent. Minor impurities neglected.

The carbonate was not taken out, for the caustic in general use contained about 5 per cent and the tests were not to be made for a special product.

They found that: silver is attacked by NaOH; gold is not attacked; copper is not attacked by NaOH at 435°C., but at 563°C. there was a noticeable reaction which increased at higher temperatures. Iron does not react with NaOH in a marked manner at 400°C., but at 700°C. the reaction is lively. After cooling, the melt appears dark red and leaves a dark-red precipitate on solution in water. Copper, on the other hand, leaves a dark-blue precipitate. Nickel does not react with NaOH at 400°C., but at higher temperatures it reacts with the formation of a green melt which yields a black residue in water.

Platinum does not react at 400°C. but is somewhat soluble around 700°C. The melt on solution in water leaves behind a black residue. Zinc acts on NaOH with generation of hydrogen, and the residue consists of  $\text{Zn}(\text{ONa})_2$ . Aluminum is slightly attacked by sodium hydroxide at temperatures ranging from 450 to 500°C. Magnesium reacts with sodium hydroxide at 400°C. in a nickel crucible in a very vigorous manner. Sodium had to be tried in a nickel crucible, since gold is dissolved in molten condition. It reacts with sodium hydroxide at 450°C. in a slight manner and more vigorously at 550°C.

B. Neumann made some experiments on mixtures of NaOH and  $\text{Na}_2\text{CO}_3$  in 1914, getting melting-point curves showing the varying current efficiencies for his mixtures. The best yields of sodium (83 per cent) were obtained on the addition of 12 to 17 per cent  $\text{Na}_2\text{CO}_3$ , the melting point of the mixture being 280°C. He also made observations on mixtures of NaOH and NaCl, but the yields were lower than with  $\text{Na}_2\text{CO}_3$  additions or with pure NaOH. In the best run only 39 per cent current efficiency was obtained, with 5.5 per cent NaCl and a melting point of 285°C. He stated that higher efficiencies in the production of sodium in technical practice could be obtained by the careful dehydration of the fused caustic before electrolysis, by the use of NaOH free from NaCl, by the addition of  $\text{Na}_2\text{CO}_3$  to lower the temperature of the bath, by

careful temperature measurements, which until now have been regarded as unnecessary, and by greater attention to the anodic separation of water.

The melting point drops from 296°C. for pure NaOH to 280°C. for the NaOH-Na<sub>2</sub>CO<sub>3</sub> mixture containing 17 per cent Na<sub>2</sub>CO<sub>3</sub>, rising again to 297°C. for 30 per cent Na<sub>2</sub>CO<sub>3</sub>.

The current efficiency rises from about 25 per cent at 2 per cent Na<sub>2</sub>CO<sub>3</sub> to a maximum of 63.03 per cent at 17 per cent Na<sub>2</sub>CO<sub>3</sub>, decreasing again to 40 per cent at 27 per cent Na<sub>2</sub>CO<sub>3</sub>.

At the maximum current efficiency the range of temperature between freezing and overheating is also a maximum, being 16°. Above this concentration of Na<sub>2</sub>CO<sub>3</sub> the temperature range gradually diminishes and a factory using these strengths can run with only low efficiencies, if at all.

The voltage between the electrodes in this mixture amounted to an average of 6 volts.

Caustic soda is found in the industries usually accompanied by some NaCl, sometimes up to 3 per cent. Naturally, in continued electrolysis the salt content increases in the cell, since the decomposition potential of salt at 300°C. (likewise that of Na<sub>2</sub>CO<sub>3</sub>) is about 1 volt higher than that of NaOH. The consequence of continued increase of salt content is poorer yields and the necessity for finally discarding the bath.

It was found that in mixtures of salt and caustic the melting point decreased from 289.3°C. with zero salt to a minimum of 283°C. with 7 per cent salt, then rose rapidly to 315°C. with a 15.6 per cent salt content.

Von Wartburg found that no chlorine was generated at the anode with mixtures containing from 25 to 50 per cent NaCl.

**Important Uses.**—Metallic sodium is a good reducing agent, and is used in the reduction of various organic compounds. On the large scale it is made into sodium peroxide for bleaching and sodium cyanide for fumigation, separating gold from its ores, and electroplating. In the form of sodamide it is used with phenyl glycine for manufacturing synthetic indigo. With lead it forms an alloy which is used on the market for the preparation of hydrogen in pure form, the mixture bearing the trade name of "hydrone." As sodium peroxide it is made up with proper amount of inert material into pellets of "oxone," which are used as a means of generating pure oxygen gas for hospital use.

**Chief Alloys and Compounds.**—Sodium-potassium alloy is used in thermometry.

**Sodium Amalgam.**—Gray pieces the size of a pea, containing 2 per cent Na, formed by adding sodium in small pieces to mercury heated to 198°C. It is used for reduction of metal haloids, detection of SO<sub>2</sub>, and preparation of hydrogen.

**Sodium Bicarbonate (Baking Soda)** (NaHCO<sub>3</sub>).—White, amorphous powder, with cooling, mildly alkaline taste and mildly alkaline reaction, soluble in water: melting point, 1098°C.

**Sodium Bisulphate** (NaHSO<sub>4</sub>·H<sub>2</sub>O).—Large, long, colorless, four-sided, triclinic crystals or grayish masses; soluble in water with decomposition; decomposed by alcohol, melting point above 315°C.; decomposes at white heat.

**Sodium Borate (Borax)** (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O).—Large, hard, monoclinic prisms, somewhat whitish, sometimes clear and colorless; slightly efflorescent; loses all its crystalline water when heated; soluble in water; solution absorbs some CO<sub>2</sub> from the air on standing; insoluble in alcohol; sweet, cooling taste; melting point, 75.5°C.



**Sodium Chlorate** ( $\text{NaClO}_3$ ).—Colorless crystals, with cooling saline taste, decomposed by heat or by strong acids, good oxidizing agent, soluble in water, soluble in cold alcohol, more easily in hot; melting point,  $302^\circ\text{C}$ .

**Sodium Chloride** (*Common Salt*) ( $\text{NaCl}$ ).—Colorless, transparent, cubic crystals; white crystalline powder, or translucent to opaque lumps with pure alkaline taste; neutral reaction; generally slightly deliquescent on account of impurities, the pure salt is only slightly hygroscopic; crackles when heated; soluble in water, with slight lowering of temperature; soluble in alcohol, the solubility increasing with the temperature; insoluble in ether; very slightly soluble in ether-absolute alcohol; melting point,  $776^\circ\text{C}$ ., volatile at higher temperatures.

**Sodium Cyanide** ( $\text{NaCN}$ ).—White, deliquescent crystals, poisonous powder, crystallizes with difficulty, soluble in water. It is manufactured by melting sodium metal with ammonia gas and passing over red-hot charcoal.

**Sodium Dichromate** ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot \text{H}_2\text{O}$ ).—Thin, hyacinth-red, deliquescent, triclinic prisms, soluble in water—more so than  $\text{Na}_2\text{CrO}_4$ ; loses its crystalline water at  $110^\circ\text{C}$ ., melts at  $320^\circ\text{C}$ ., and decomposes at  $400^\circ\text{C}$ .

**Sodium Fluoride** ( $\text{NaF}$ ).—Clear, colorless, lustrous, sometimes opalescent, cubical crystals, with alkaline reaction; more bitter taste than  $\text{KF}$ ; decrepitates when heated; very slightly soluble in cold water; heating does not increase solubility; almost insoluble in alcohol, melting point,  $902^\circ\text{C}$ .

**Sodium Hydroxide** (*Caustic Soda Lye*) ( $\text{NaOH}$ ).—White, hard, brittle, very deliquescent sticks or amorphous powder, with strong alkaline reaction; absorbs  $\text{CO}_2$  from the air; dissolves in water with evolution of great heat; easily soluble in alcohol, wood spirit, or glycerin; somewhat soluble in ether, melts below red heat, volatilizes at very bright red heat or higher than  $\text{KOH}$ . In electrochemistry it is the raw material of the Castner process for the manufacture of metallic sodium.

**Sodium Nitrate** (*Chile Salt-peter*) ( $\text{NaNO}_3$ ).—Colorless, slightly deliquescent, transparent, rhombohedral crystals, that are nearly cubical, with saline, slightly bitter taste; soluble in water, with lowering of temperature; soluble in solutions of several salts of alkali metals; soluble in alcohol; melting point,  $316^\circ\text{C}$ .

**Sodium Perborate** ( $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ ).—White crystals with about 10 per cent active oxygen, soluble in about 40 parts of water at  $20^\circ\text{C}$ ., with slightly alkaline reaction; liberates  $\text{H}_2\text{O}_2$  with dilute acids; decomposed by concentrated  $\text{H}_2\text{SO}_4$  with formation of ozone; evolves oxygen when heated to above  $60^\circ\text{C}$ .; is decomposed by catalyzers, ferments, and animal tissues.

**Sodium Peroxide** ( $\text{Na}_2\text{O}_2$ ).—Yellowish-white, amorphous powder; deliquesces gradually in air and absorbs  $\text{CO}_2$ , forming solid  $\text{Na}_2\text{CO}_3$ ; easily soluble in water, with evolution of much heat, and formation of  $\text{NaOH}$ ; a good oxidizing agent; evolves oxygen when heated. It is prepared by subjecting small pieces of metallic sodium to dry air heated to about  $300^\circ\text{C}$ .

**Sodium Persulphate** ( $\text{Na}_2\text{S}_2\text{O}_8$ ).—White, crystalline powder, soluble in water, strong bleacher and antiseptic like the potassium salt.

**Ammonium** ( $\text{NH}_4$ ).—This is a radical that acts like an atom of a univalent metal. It has never been isolated, and is known only in combination with acid radicals in ammonium salts, which give no flame coloration. It occurs in small amounts as carbonate and nitrate in the air, as ammonium chloride in the fissures of active volcanoes. Ammonium derivatives are formed by the decay of many organic substances containing nitrogen, albumen, and urea, and in a similar way by the dry distillation of many nitrogenous substances, such as coal, horn, and hair.

**Caesium** (Cs, atomic weight, 132.9; specific gravity, 1.88; melting point, 26°C.).—It is a silvery-white, soft, ductile metal, oxidizing easily and rapidly in air, with the production of heat and light. It decomposes water violently at ordinary temperatures, with ignition of the hydrogen evolved. It was the first metal to be discovered with the spectroscope and is distinguished by two bright-blue lines in the spectrum. It is one of the softest of metals, and has the following electrical conductivity:

Solid at 19.3°C .....  $4.74 \times 10^4$  reciprocal ohms

Liquid at 30°C .....  $2.73 \times 10^4$  reciprocal ohms

Liquid at 37°C .....  $2.70 \times 10^4$  reciprocal ohms

Heat of formation of CsOH, 101.31 cal.

Caesium is not a rare element, strictly speaking—it is found almost everywhere, though in small amounts. It replaces potassium in many feldspars and micas, as well as in many rocks carrying these minerals and the waters oozing from them. Pollucite, a mineral closely related to leucite, found at Elba, and crystallizing in the regular system, is a typical caesium mineral, having the composition  $(\text{SiO}_3)_3 \cdot \text{Al}_4\text{Cs}_4\text{H}_2$ .

**Metallurgy.**—The best source of caesium is the residue left after the extraction of lithium salts from lepidolite. This residue consists of sodium, potassium, and lithium chlorides, together with small quantities of caesium and rubidium chlorides. The latter are separated from the rest by repeated fractional crystallization of their double platinum chlorides, which are much less soluble in water than those of the other alkali metals. Reduction of the mixture by hydrogen and extraction by water yield the caesium and rubidium chlorides.

Other means of separating the two from the more common alkalis are to convert them into double chlorides with stannic chloride, and into alums, which are very slightly soluble in a solution of potash alum. In order to separate caesium from rubidium, use is made of the different solubilities of their various salts. The bitartrates and alums have been tried, also the double chloride of caesium and antimony, the corresponding compound not being formed by rubidium. Caesium is also obtained by heating the hydroxide with magnesium or aluminum, as well as by heating the chloride with metallic calcium. In the latter case a special V-shaped tube is used, and the reaction starts between 400 and 500°C. The metal has also been obtained by electrolysis of a mixture of caesium and barium cyanides.

**Chief Compounds.**—*Caesium Bromide* ( $\text{CsBr}$ ).—Colorless, crystalline powder; used in nervous heart palpitation.

*Caesium Carbonate* ( $\text{Cs}_2\text{CO}_3$ ).—White, deliquescent, crystalline powder; used in brewing and in the manufacture of mineral waters.

*Caesium Chloride* ( $\text{CsCl}$ ).—Colorless crystals, also used in brewing and the manufacture of mineral waters.

*Caesium Hydroxide* ( $\text{CsOH}$ ).—Colorless or yellowish, very deliquescent crystalline mass, with strongly alkaline reaction.

*Caesium Sulphate* ( $\text{Cs}_2\text{SO}_4$ ).—Colorless, prismatic crystals; used in brewing and in the manufacture of mineral waters.

**Rubidium** (Rb, atomic weight, 85.4; specific gravity, 1.52; melting point, 38.5°C.).—It is a silvery-white metal, oxidizing rapidly on exposure to air, and

decomposing water very rapidly. It closely resembles caesium and potassium in its general properties. The rubidium salts are generally colorless, mostly soluble in water, and isomorphous with the corresponding potassium salts.

Rubidium is found in the minerals lepidolite, petalite, and in various specimens of mica and of carnallite, and in some mineral waters. It also occurs in tea, cocoa, coffee, tobacco, and in the ashes of beet root. It was discovered in the spectroscopic examination of the residues obtained on evaporation of water from a mineral spring at Dürkheim, being characterized by two distinctive red lines, which give it the name. The best source of rubidium salts is the residue left after extracting lithium salts from lepidolite, the method of separation being based on the different solubilities of the platinichlorides of potassium, rubidium, and caesium in water.

Rubidium is prepared by distilling the carbonate with carbon (an explosive compound similar to that obtained from potassium and carbon monoxide is likely to be formed simultaneously); also by reducing the hydroxide with aluminum, reducing the hydroxide with magnesium, and by heating the fused chloride with calcium in an exhausted glass tube at 400 to 500°C. The fused chloride has been electrolyzed in a nickel vessel, with an iron-wire cathode and an iron-cylinder anode. The product on cooling was opened under pyridine cooled by a freezing mixture. Further notes on rubidium metallurgy will be found on p. 1403.

**Chief Compounds.** *Rubidium Bromide* (RbBr).—Colorless, crystalline powder, soluble in water, and used for epilepsy, delirium tremens, headache, and insomnia, as potassium bromide is used.

*Rubidium Carbonate* (Rb<sub>2</sub>CO<sub>3</sub>).—Deliquescent crystals or deliquescent white powder, soluble in water and acids.

*Rubidium Hydroxide* (RbOH).—Grayish-white deliquescent mass, soluble in water and acids; used in manufacture of glass.

*Rubidium Tartrate* (RbC<sub>4</sub>H<sub>6</sub>O<sub>6</sub>).—Colorless crystals, soluble in water; used for nervous palpitation.

**Lithium** (Li, atomic weight, 7.0; specific gravity, 0.59; melting point, 180°C.) It is a silvery-white, soft metal readily oxidized on exposure to the air. It burns on ignition in air, and when strongly heated in nitrogen atmosphere forms lithium nitride (Li<sub>3</sub>N). It decomposes water at ordinary temperatures, causing the evolution of hydrogen and the formation of lithium hydroxide.

Electrical conductivity of lithium:

At 20°C.  $11.4 \times 10^4$  reciprocal ohms, or about 20.4 per cent of conductivity of hard silver.

At 230°C.:

Solid lithium.....	$7.88 \times 10^4$ reciprocal ohms
Liquid lithium.....	$2.21 \times 10^4$ reciprocal ohms

Spectrum has two sharply defined lines, a weak yellow line, Li $\beta$  of wave length 6,104, and a bright red line, Li $\alpha$  of wave length 6,708.

It is only found in combination, and is a constituent of the minerals petalite, triphylite, spodumene, and lepidolite or lithia mica. It occurs in small quantities in sea, river, and spring water, and is also widely but very sparingly distributed throughout the vegetable kingdom.

It may be obtained in the form of its chloride by fusing lepidolite with a mixture of barium carbonate and sulphate and potassium sulphate. The fused mass separates

into two layers, the upper of which contains a mixture of potassium and lithium sulphates, which is lixiviated with water and converted into the mixed chlorides by adding barium chloride, the solution evaporated and the lithium chloride extracted by a mixture of dry alcohol and ether. It is obtained as metal by heating dry lithium hydroxide with magnesium. It may also be made by electrolyzing the chloride in pyridine solution with a carbon anode and an iron or platinum cathode. Another process is to electrolyze a mixture of bromide and chloride which has a melting point of 520°C.

**Chief Compounds.**—*Lithium Bromide* (LiBr).—White, deliquescent, slightly bitter, granular powder, soluble in water.

*Lithium Carbonate* ( $\text{Li}_2\text{CO}_3$ ).—Light, white, alkaline powder, soluble in water and dilute acids, insoluble in alcohol.

*Lithium Chloride* (LiCl).—Colorless, deliquescent, crystals, with sharp alkaline taste. It is used the same as the carbonate, also in pyrotechnics and in the manufacture of mineral waters.

*Lithium Hydroxide* (LiOH).—White, caustic powder, with acrid alkaline taste; melting point 445°C.; heat of formation, 111.0 cal. Used in certain types of storage batteries.

*Lithium Iodide* (LiI).—White, deliquescent coarse powder, soluble in water.

*Lithium Nitrate* ( $\text{LiNO}_3$ ).—Deliquescent, transparent crystals, soluble in water and alcohol.

*Lithium Sulphate* ( $\text{Li}_2\text{SO}_4$ ).—Colorless crystals.

*Lithium Cyanide* (LiCN).—White crystals, used in Roentgen ray experiments.

**The Alkaline Earths. Calcium, Strontium, Barium, Together with Beryllium.**

The metals of the alkaline-earth group are bivalent and heavier than water, which they decompose slowly at ordinary temperatures, with the evolution of hydrogen and the formation of difficultly soluble hydroxides of strongly alkaline reaction. The salts are mostly colorless and insoluble in water. The halogen compounds, nitrates, nitrites, and acetates, are soluble in water. The carbonates are insoluble in water and are decomposed on ignition into carbon dioxide and white, infusible, strongly luminous metallic oxides:  $\text{RCO}_3 = \text{RO} + \text{CO}_2$ .  $\text{BaCO}_3$  is an exception to the general rule. It loses its  $\text{CO}_2$  only when heated to a white heat, and the oxide is not very luminous.

The sulphates and the oxalates are very difficultly soluble, the barium sulphate being the most insoluble and calcium sulphate the most soluble. Of the oxalates the calcium salt is the most insoluble. The metals of this group form oxides of the general type  $\text{RO}$ , and peroxides corresponding to the formula  $\text{RO}_2$ . The latter, on treatment with acids, give hydrogen peroxide and salts corresponding to the oxide  $\text{RO}$ :  $\text{RO}_2 + 2\text{HCl} = \text{RCl}_2 + \text{H}_2\text{O}_2$ .

**Calcium**<sup>1</sup> (Ca, atomic weight, 40.07; specific gravity, 1.578; melting point, 810°C.; boiling point, 1400°C. (?); hardness on Rynabey scale, 1.5 (Mg = 2, Sn = 1.8, Pb = 1.5, K = 0.5).—Tends to clog a file or saw, but can be easily turned, hammered cold into thin sheets, and swaged into rods. Tensile strength about 512 kg. per square centimeter; heat of combustion per gram equivalent, 80.097 cal.; specific heat between -180 and +20°C., 0.1574. It is a lustrous silvery-white metal that oxidizes easily and quickly tarnishes to yellow in air, it decomposes water with the evolution of  $\text{H}_2$ . Calcium salts color the bunsen flame orange.

<sup>1</sup> Acknowledgment is here made to Dr C Dantszen of the General Electric Co. for use of his personal notes on calcium.—EDITOR.

Calcium is widely distributed in nature. It is found in enormous deposits in all stratified formations as carbonate (limestone, marble, chalk), often rich in petrifications. The carbonate ( $\text{CaCO}_3$ ) is dimorphous, crystallizing in rhombohedrons as calcite and in the orthorhombic system as aragonite. Calcium also occurs in large masses as sulphate, partly as monoclinic crystallizing gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), and partly as anhydrite ( $\text{CaSO}_4$ ), which crystallizes in the orthorhombic system. Calcium also occurs as fluorite ( $\text{CaF}_2$ ), which crystallizes in the isometric system with perfect octahedral cleavage; as apatite,  $\text{Ca}_4(\text{PO}_4)_3\text{CaCl}$ , which belongs to the hexagonal system; and, finally, in innumerable silicates, such as the monoclinic wollastonite ( $\text{CaSiO}_3$ ), and the triclinic anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ). The calcium minerals are the chief representatives of several important isomorphous groups.

Calcium is one of the most important of the metals in the arts. As the metallic element alone it is made into an alloy with lead, for use in certain bearings.

It is a powerful reducing agent, and is used to limited extent as a deoxidizer and for removing nitrogen from alloys. It acts also as an absorbent for gases,  $\text{H}_2$  and  $\text{N}_2$  in gas analysis, is a constituent of light aluminum alloy, and is a hardening component in certain lead-base antifriiction alloys.

Its average compressibility at  $20^\circ\text{C}$ ., is  $5.7 \times 10^{-6}$  between 100 and 500 megabars per square centimeter. Its specific electrical resistance at  $0^\circ\text{C}$ . is 3.43 microhms per centimeter cube; temperature coefficient, 0.00457 per degree Centigrade; electrical conductivity at  $20^\circ\text{C}$ ., 45.1 compared with silver at 100; heat of hydration of calcium ions, 344 cal.; ionic radii of calcium ions, 1.25 Å. Calcium vapor is not ionized by heating to  $700^\circ\text{C}$ . Pure calcium is passive toward  $\text{N}_2$ . When heated in hydrogen, calcium hydride is formed. Calcium can abstract sulphur and phosphorus from iron. Calcium is vigorously attacked by fluorine at ordinary temperatures. At  $400^\circ\text{C}$ . chlorine attacks it with incandescence.

Heated to dull redness in  $\text{HCl}$  gas, calcium glows and forms  $\text{CaCl}_2$ . Sodium dissolves calcium at high temperatures and calcium crystallizes out again on cooling, forming two layers. Calcium forms brittle alloys with Mg, Zn, and Ni, which decompose  $\text{H}_2\text{O}$ . Calcium vigorously attacks Sn, but the alloy retains only a little calcium. It does not alloy to large extent with Pb or Sn. Rubbed up with Hg it forms an amalgam. Alkali oxides, Na, K, and Li, are reduced to metals by calcium on heating. Alkali hydroxides are also reduced with detonation. At  $300^\circ\text{C}$ . it reacts with sulphur to form  $\text{CaS}_2$ .

**Metallurgy.**—A great many attempts have been made, but unsuccessfully, to obtain the metal by chemical means, although almost pure metal can be made by reducing the iodide with metallic sodium.<sup>1</sup> Electrolysis with calcium chloride solution and a mercury cathode yields an amalgam very difficult to separate, and the resulting calcium is a powder. Calcium has been obtained by electrolyzing a fused mixture of sodium and calcium chlorides, also with calcium iodide at a low red heat, using a nickel cathode and graphite anode. The most important process, used commercially, consists in the electrolysis of calcium chloride or a mixture with fluorspar, with a graphite anode in a fire-brick vessel.

However, it may be noted here that, while Wohler recommends an electrolyte of 100 parts  $\text{CaCl}_2$  and 17 parts  $\text{CaF}_2$ , and this electrolyte was apparently adopted in the Rathenau process, Frary, Bicknell, and Tronson concluded in 1909 that pure  $\text{CaCl}_2$  free from water and all other halides, was superior to the chloride-fluoride mix.<sup>2</sup>

<sup>1</sup> MOISSAN, *Compt. rend.*, (1898), 1753–1758

<sup>2</sup> *Trans. Am. Electrochem. Soc.*, **16** (1909), 185–195

Bunsen is said to have prepared calcium as early as 1854 by electrolyzing an aqueous solution of the chloride with a mercury cathode and then distilling off the mercury.<sup>1</sup> Calcium is soluble in molten but not in solid sodium, so that if calcium iodide and a considerable excess of sodium be heated together in a steel container at approximately 750°C., the iodide is reduced and dissolves in the metallic sodium, from which it

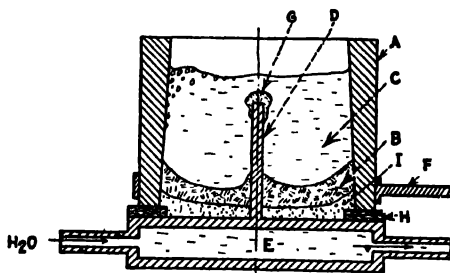


FIG. 6.—Submerged cathode cell.

crystallizes on cooling. The remaining sodium is removed with absolute alcohol, and Moissan says the product is 99.2 per cent pure.

The earlier attempts at a large-scale production resulted in the development by Borchers and Stockem of what may be designated as the "submerged cathode" type of cell. Fig. 6 is a diagrammatic representation of such a cell. A graphite shell, A,

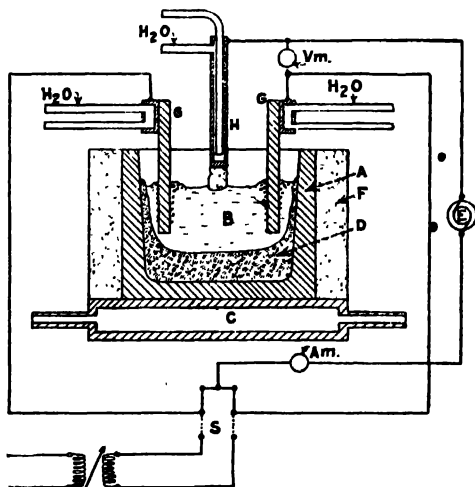


FIG. 7.—Improved Rathenau cell.

is closed at the bottom by a water-cooled plate, *E*, to which is fastened the upright, water-cooled cathode, *D*, concentric with *A*. The shell and cooling plate are separated by an insulating ring, *H*, of asbestos or mica. Electrical connections are made to the cooler plate and to the graphite shell, as at *F*. The floor of the cell is covered with a layer of powdered calcium oxide or calcium fluoride, *I*.

<sup>1</sup> *Ann. Phys.*, **92** (1854), 251.

Operation of the cell is started by filling it with molten calcium chloride and electrolyzing. The calcium collects as at *G*, on the central cathode, and the chlorine is evolved at the inner surface of the graphite shell. The cooler plate maintains a layer of solid calcium chloride, *B*, on the bottom of the cell. The originators of this cell operated it under such conditions of current density and temperature that a sponge of calcium was formed about the cathode. This sponge was compacted by pressing and the chloride removed. The calcium content of the resulting mass was from 50 to 90 per cent.

Rathenau developed an improved type of cell based on building up a rod of calcium by using a cooled cathode that just touches the surface of the fused electrolyte and moving the cathode up as the electrolyzed metal accumulates on it.

A diagrammatic representation is given in Figure 7. *A* is a graphite container for the fused electrolyte, *B*, which is cooled on the bottom by a water-jacket, *C*. This maintains a solid mass of electrolyte, *D*, on the bottom. A jacket, *F*, of fine graphite and lamp black protects the container *A*. Two water-cooled graphite plates, *G*, *G'*, form the anodes. *H* is the cathode.

On electrolysis a layer of metallic calcium is formed at the lower end of this rod on the surface of the electrolyte; the rod is gradually raised by means of a small shunt-wound direct-current motor, *E*, with variable speed, the thickness of the layer increases, and ultimately a rod of metallic calcium is formed as a continuation of the iron cathode. The bath is warmed at the start by means of current from a 60-cycle induction regulator. The electrolyte is at a higher temperature near the cathode than the bath proper. The thickness of the calcium rod is kept at about 2 mm. by the adjustment of the motor speed to the resistance of the calcium electrode.

With too low temperature, calcium is formed in a voluminous spongy mass. This condition is obviated by raising the anodes slightly to raise the temperature. Too high temperature causes too much calcium to remain molten and requires rapid regulation to avoid arcing. The anode effect is not troublesome unless the current density exceeds the critical value. Anhydrous calcium chloride is found best and is obtained by dissolving pure calcium chloride in a little water, adding a small amount of ammonium chloride, boiling to solidification, and then dehydrating after adding further ammonium chloride in a muffle at 400°C. Treating the fused salt in the cell with a small amount of metallic calcium before electrolysis has helped to start the action. Rods 35 cm. long and 7.5 mm. in diameter are obtained. These rods may be made into wire or sheet by forging and rolling either hot or cold. Brief annealing at 350°C. removes the brittleness due to excessive work. The metal is extremely plastic between 300 and 400°C. and analysis shows about 1.08 per cent Cl, etc.

Cold-rolled metal has a specific gravity of 1.46 and a resistivity of 6.77 microhms per centimeter cube at 22°C.

The electrolysis of  $\text{CaCl}_2$  is carried on at a temperature very little above its melting point, 800°C. The heat due to the current is sufficient to keep salt melted in the upper part of the cell. The current density is 9.3 amp. per square decimeter. Average voltage, 25, and ampere efficiency is better than 80 per cent.

The energy efficiency was 80 times  $\frac{3.24}{25}$  equals 10 per cent where 3.24 equals the decomposition voltage of fused  $\text{CaCl}_2$  at 800°C.; 1 kg. of calcium requires 42 kw.-hr.

Calcium is also produced by the electrolysis of fused  $\text{CaCl}_2$  with 15 per cent KCl. The current density is 60 to 110 amp. per square decimeter. The ampere efficiency is 75 to 90 per cent. An electrolyte of  $\text{CaCl}_2$  with 60 per cent KCl did not give a coherent stock of calcium, probably due to an alloy of calcium and potassium. P. H. Bruce<sup>1</sup> gives the following for a 500-amp. Rathenau cell.

<sup>1</sup> *Chem Met Eng*, July 20, 1921.

## CONTAINER, ACHESON GRAPHITE

Outside diameter . . . . .	12 in.
Inside diameter:	
Top . . . . .	11 in.
Bottom . . . . .	10½ in.
Depth . . . . .	9 in.
Total workable anode area . . . . .	80 sq. in.
Average running area. . . . .	60 sq. in.
Charge. . . . .	25 to 35 lb.
Cell works at 25 to 30 volts and 400 to 500 amp.	

But it may be noted that in a graphite cell there is a tendency for the graphite to flake off and come in contact in the cell with the fused calcium, forming carbide, and thus contaminating the calcium. Therefore fire brick with two embedded electrodes is now considered preferable. A good rate of lift in practice has been found to be 0.05 to 0.1 cm. per minute.

During the first 20 min. of the electrolysis no calcium is formed, hydrogen gas being given off at the cathode. It appears to be impossible to produce calcium chloride without some calcium oxychloride ( $\text{CaOHCl}$ ), and until this is decomposed by electrolysis no calcium forms.

**Chief Alloys and Compounds.**—Calcium can be used to reduce the oxides of many of the rare metals—U, Zr, V, and Ti, for example—the so-called Wedekind reactions.<sup>1</sup> It is also used in the hot-cathode rectifier to clean up the argon gas.

**Calcium Bisulphate** ( $\text{CaSO}_3$  dissolved in  $\text{H}_2\text{SO}_4$  solution).—A liquid with strong sulphur dioxide odor used largely in the manufacture of sulphite cellulose and in paper making.

**Calcium Bromide** ( $\text{CaBr}_2$ ).—White, very deliquescent lumps or needles, with silky luster, sharp saline taste, very soluble in water or alcohol, absorbs  $\text{NH}_3$ .

**Calcium Carbide** ( $\text{CaC}_2$ ).—Grayish-black, irregular lumps, decomposed by water, with evolution of acetylene gas, and residue of slaked lime. The acetylene formed may be taken up by acetone, which will hold 60 per cent of its weight of the gas in solution. Specific gravity, 2.22. It is used for the generation of acetylene gas for lighting purposes (1 kg. of carbide yields 280 to 300 l. of acetylene), as a reducing agent—as for direct reduction of copper sulphide to metallic copper—as signal fires for marine service, and in the manufacture of calcium cyanide in the fertilizer industry.

**Calcium Carbonate** (Limestone, Marble, and so forth) ( $\text{CaCO}_3$ ).—Native crystalline  $\text{CaCO}_3$  varies from thin tubular to long, prismatic crystals, and from transparent to opaque. Calc spar is generally colorless, in hexagonal rhombohedra; aragonite, colorless, trimetric, right rhombic prisms; marble, massive and crystalline; chalk and precipitated  $\text{CaCO}_3$ , fine, white, or gray amorphous lumps or powder, slightly soluble in  $\text{NH}_4\text{Cl.Aq.}$ , soluble in  $\text{H}_2\text{CO}_3\text{.Aq.}$ ; soluble in dilute  $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{HC}_2\text{H}_3\text{O}_2$  with the evolution of  $\text{CO}_2$ ; similarly decomposed by  $\text{H}_2\text{SO}_4$ , but leaving insoluble  $\text{CaSO}_4$ ; decomposed at full red heat into  $\text{CaO}$  and  $\text{CO}_2$ .

**Calcium Chlorate** ( $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{H}_2\text{O}$ ).—Very deliquescent, colorless, rhombic prisms; very soluble in water or alcohol; decomposes with evolution of  $\text{O}_2$  when heated slowly; melts at about  $100^\circ\text{C.}$  in its water of crystallization when heated rapidly.

**Calcium Chloride** ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ).—Colorless, very deliquescent, hexagonal, prismatic crystals; very soluble in water; melting point,  $30^\circ\text{C.}$ , boiling point,  $723^\circ\text{C.}$  In the anhydrous form it is composed of white, deliquescent, fibrous masses or dull lumps; the fused salt has a crystalline structure and alkaline reaction; is very soluble in water or alcohol.

<sup>1</sup> *Am. Chem.*, **395**, (1913), 149–194.



**Calcium Fluoride** ( $\text{CaF}_2$ ).—White or grayish-white, fine powder, well-formed cubes; occurs in nature; insoluble in water, soluble in solutions of  $\text{NH}_4$  salts; soluble in cold concentrated  $\text{HCl}$ ,  $\text{HF}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HNO}_3$ , but reprecipitates when the solutions are diluted; soluble in hot dilute  $\text{HCl}$ ; decomposed by hot  $\text{H}_2\text{SO}_4$ , with evolution of  $\text{HF}$ ; the dry salt melts without decomposition at  $900^\circ\text{C}$ .

**Calcium Hydroxide** (*Water Slaked Lime*,  $\text{Ca}(\text{OH})_2$ ).—Generally found as white, or grayish-white, amorphous powder or lumps, rarely found as colorless, six-sided prisms or tablets, with strong alkaline reaction; slightly soluble in water, forming colorless, alkaline solution, called limewater; less soluble than  $\text{SrO}_2\text{H}_2$ , more than  $\text{MgO}_2\text{H}_2$ ; soluble in  $\text{NH}_4\text{Cl}$  aq.; alcohol dissolves only traces; when moist it absorbs  $\text{CO}_2$  from the air, forming  $\text{CaCO}_3$ ; does not melt, but yields  $\text{CaO}$  and  $\text{H}_2\text{O}$  at bright red heat.

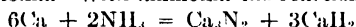
**Calcium hydride** forms at about  $700^\circ\text{C}$ . when calcium oxide is heated in a current of hydrogen. This compound reacts with water, liberating hydrogen. It has been used as a portable source of hydrogen for balloons.

**Calcium Iodide** ( $\text{CaI}_2$ ).—Yellowish-white, hygroscopic masses, white powder, or colorless tablets; absorbs  $\text{CO}_2$  and decomposes in air; very soluble in water or alcohol.

**Calcium Nitrate** ( $\text{Ca}(\text{NO}_3)_2 \cdot \text{Aq.}$ ).—Colorless, six-sided, monoclinic crystals, or white to yellowish white, radiated, deliquescent crystalline masses; very soluble in water, with evolution of much heat; soluble in glacial  $\text{HC}_2\text{H}_3\text{O}_2$ , insoluble in  $\text{HNO}_3$ ; nearly insoluble in alcohol; melts at  $44^\circ\text{C}$ .; boils at  $132^\circ\text{C}$ ., remaining clear until about one-third of the crystalline water has gone, when the anhydrous salt is deposited. Anhydrous  $\text{Ca}(\text{NO}_3)_2$  melts at  $561^\circ\text{C}$ ., decomposes at higher temperatures, leaving a phosphorescent mass.

The anhydrous nitrate, obtained by heating the crystallized salt, is very phosphorescent, and constitutes "Baldwin's phosphorus."

**Calcium nitride** is formed by contact between calcium and nitrogen above  $300^\circ\text{C}$ . At  $900^\circ\text{C}$ . the reaction is rapid, the red-brown  $\text{Ca}_3\text{N}_2$  being formed, which reacts with water to form ammonia. With ammonia the reaction is



Liquid anhydrous ammonia dissolves calcium, forming calcium-ammonium.

**Calcium Oxide** (*Quicklime*, *Burnt Lime*) ( $\text{CaO}$ ).—Occasionally lustrous cubes, generally hard; alkaline, infusible, white, or grayish-white lumps that gradually crumble on exposure to air; absorbs  $\text{H}_2\text{O}$  and  $\text{CO}_2$  on standing; decomposed by  $\text{H}_2\text{O}$ , evolving much heat and forming  $\text{CaO}_2\text{H}_2$ , which is slightly soluble; reacts with most acids to form salts; does not change to  $\text{CaO}_2$  when heated, but becomes incandescent (so-called limelight).

**Calcium Phosphate** ( $\text{Ca}_3(\text{PO}_4)_2$ ).—Light, white, odorless, tasteless, amorphous powder or masses, nearly insoluble in cold water; slowly decomposed by boiling water into a basic phosphate; soluble in  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{HC}_2\text{H}_3\text{O}_2$ ,  $\text{H}_2\text{SO}_4$ , and in solutions of  $\text{NH}_4$  salts; insoluble in alcohol; decomposed by  $\text{H}_2\text{SO}_4$ .

**Calcium Sulphate** ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).—Transparent to white, six-sided, monoclinic prisms, or white powder; very slightly soluble in water; loses its crystalline water at  $80^\circ\text{C}$ ., the anhydrous salt then sets up in a hard mass.

**Calcium Sulphide** ( $\text{CaS}$  aq.).—Grayish or yellowish-white, amorphous powder with  $\text{H}_2\text{S}$  odor; phosphorescent; sparingly soluble in water with partial decomposition,  $\text{H}_2\text{S}$  being evolved; soluble in acids; does not melt when heated. It is used in the preparation of luminous objects, such as match boxes, clock faces, and plates for house numbers, also for preparing As-free  $\text{H}_2\text{S}$ .

**Calcium Sulphite** ( $\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$ ).—Small, lustrous crystals, or white powder that oxidizes slowly to  $\text{CaSO}_4$  on standing; insoluble in water, soluble in  $\text{H}_2\text{SO}_3$ ; loses its crystalline water at  $100^\circ\text{C}$ .; decomposed by heat.

**Calcium Tungstate** ( $\text{CaWO}_4$ ).—Fine powder or quadratic octahedra; insoluble in water, or dilute acids; decomposed by boiling mineral acids, with separation of

canary-yellow  $\text{WO}_3$ . It is used in varying degrees of fineness for preparing screens for taking photographs by the Roentgen rays.

**Strontium** (Sr, atomic weight, 87.62; specific gravity, 2.54; melting point,  $800^\circ\text{C}$ ).—It is probably never obtained pure, but is said to be a yellowish white, malleable, ductile, metallic element, somewhat harder than calcium or barium, which can be beaten into thin leaves, oxidizes easily on exposure to air, decomposes in cold water, with the evolution of  $\text{H}_2$ . Fusible strontium salts color the bunsen flame red, somewhat similar to the lithium red. Strontium melts at red heat and is volatile only at extremely high temperatures. With dry  $\text{NH}_3$  at  $60^\circ\text{C}$ . the metal forms strontium ammonium, which slowly decomposes in a vacuum at  $20^\circ\text{C}$ . giving  $\text{Sr}(\text{NH}_3)_2$ ; with CO it gives  $\text{Sr}(\text{CO})_2$ ; with oxygen it forms the monoxide and peroxide; and with  $\text{HNO}_3$  it forms the hyponitrite.

Strontium occurs quite commonly with calcium, but usually in much smaller amounts. There are only a few real strontium minerals. The most important of these are: strontianite ( $\text{SrCO}_3$ ), orthorhombic, isomorphous with aragonite; and celestite ( $\text{SrSO}_4$ ), orthorhombic, isomorphous with barite. The metal as such is not in common use at present.

**Metallurgy.**—The metal has been obtained by heating the hydride in a vacuum to  $1000^\circ\text{C}$ . The hydride was made by heating strontium amalgam in a current of hydrogen. Strontium amalgam can be obtained by electrolyzing an aqueous solution of strontium chloride with a mercury cathode, a liquid and a solid amalgam ( $\text{SrHg}_{11}$ ) being formed. This amalgam is heated and gives a mixture of  $\text{Sr}_2\text{Hg}_8$  and  $\text{SrHg}_6$ , and an amalgam passes over on distillation. The metal has also been isolated by electrolysis of the moist hydroxide or chloride.

**Chief Alloys and Compounds.**—*Strontium Acetate* ( $\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{Aq.}$ ).—White, crystalline powder, soluble in water.

*Strontium Bromide* ( $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ ). Long, deliquescent, colorless or white needles, with bitter, saline taste; soluble in water, slightly soluble in absolute alcohol; melts in its crystalline water; absorbs  $\text{NH}_3$ .

*Strontium Carbonate* ( $\text{SrCO}_3$ ).—Colorless or white, triclinic, rhombic crystals resembling hexagonal pyramids, or white, very fine, amorphous powder; insoluble in water; slightly soluble in  $\text{NH}_4\text{Cl} \cdot \text{Aq.}$ ; soluble in  $\text{NH}_4\text{NO}_3 \cdot \text{Aq.}$  and  $\text{H}_2\text{CO}_3 \cdot \text{Aq.}$ ; soluble in dilute  $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{HC}_2\text{H}_3\text{O}_2$  with evolution of  $\text{CO}_2$ ; begins to decompose at  $820^\circ\text{C}$ ., losing  $\text{CO}_2$  slowly at  $1100^\circ\text{C}$ ., but rapidly and more completely at white heat.

*Strontium Chloride* ( $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ).—White, hexagonal needles or powder, with sharp, bitter taste; soluble in water, insoluble in alcohol; used in the manufacture of carbonate, and to some extent for red flames (in alcoholic solution).

*Strontium Dioxide* ( $\text{SrO}_2 \cdot 8\text{H}_2\text{O}$ ).—White powder, melts at red heat, slightly soluble in water, easily soluble in acids or  $\text{NH}_4\text{Cl} \cdot \text{Aq.}$ , insoluble in  $\text{NH}_4\text{OH}$ . Used for bleaching.

*Strontium Hydroxide* ( $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ).—Small, transparent, colorless, deliquescent, quadratic crystals, or fine, white powder; soluble in water, forming an alkaline solution, less soluble than  $\text{Ba}(\text{OH})_2$ , more than  $\text{Ca}(\text{OH})_2$ ; soluble in cold  $\text{NH}_4\text{Cl} \cdot \text{Aq.}$ ; absorbs  $\text{CO}_2$  from the air, forming  $\text{SrCO}_3$ ; loses all its crystalline water at  $100^\circ\text{C}$ ., then melts at higher heat, and finally yields  $\text{SrO}$  and  $\text{H}_2\text{O}$ . It is used technically in the sugar industry for separating crystallizable sugar from molasses, and in the manufacture of caustic alkalis from corresponding carbonates.

**Strontium Iodide** ( $\text{SrI}_2 \cdot 6\text{H}_2\text{O}$ ).—White or slightly yellow, finely crystalline, deliquescent powder, or almost colorless hexagonal plates, with saline, slightly bitter taste; soluble in water.

**Strontium Oxide** ( $\text{SrO}$ ).—Grayish-white, porous, infusible, caustic masses, occasionally regular cubes; absorbs  $\text{CO}_2$  from the air, with the formation of  $\text{SrCO}_3$ ; soluble in water, with the evolution of heat and the formation of alkaline solution of  $\text{Sr}(\text{OH})_2$ ; very slightly soluble in alcohol.

**Strontium Phosphate** ( $\text{Sr}_3(\text{PO}_4)_2$ ).—White powder, amorphous or crystalline; insoluble in water; decomposes when boiled with water; soluble in  $\text{HCl}$  and  $\text{H}_3\text{PO}_4$ . *Aq.*

**Strontium Nitrate** ( $\text{Sr}(\text{NO}_3)_2$ ).—White powder used in pyrotechnics (red fire).

**Strontium Sulphate** ( $\text{SrSO}_4$ ).—Colorless, rhombic crystals, when native; when precipitated, it is a fine, white, amorphous powder. It is insoluble in water; sparingly soluble in  $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{HC}_2\text{H}_3\text{O}_2$ ; soluble in hot, concentrated  $\text{H}_2\text{SO}_4$ ; insoluble in  $\text{NH}_4\text{Cl}$ . *Aq.*; melts when strongly heated; decomposes at white heat. It is used in pyrotechnics.

**Strontium Sulphide** ( $\text{SrS}$ ).—White powder that turns yellowish, slowly on exposure to air; soluble in water, with decomposition; soluble in acids; phosphoresces like  $\text{BaS}$ . Two polysulphides exist,  $\text{SrS}_4$  and  $\text{SrS}_8$ . It is used in luminous paints, because of its phosphorescent properties.

**Strontium peroxide** ( $\text{SrO}_2$ ) can be prepared over 85 per cent pure by heating  $\text{SrO}$  at 400 to 500°C. with oxygen at a pressure of 1,500 to 1,800 lb. per square inch.<sup>1</sup>

**Barium** ( $\text{Ba}$ , atomic weight, 137.37; specific gravity, 3.6).—Melts at red heat, higher than cast iron, but cannot be distilled; burns in the oxyhydrogen flame. It probably never has been obtained pure; said to be a yellow, slightly lustrous, somewhat malleable, somewhat metallic element; oxidizes easily in air; decomposes cold water, with the evolution of  $\text{H}_2$ . Fusible barium salts color the bunsen flame yellowish green.

Like strontium, barium is almost always found associated with calcium, but only in small quantities. The most important barium minerals are: witherite ( $\text{BaCO}_3$ ), orthorhombic, isomorphous with aragonite; barite or heavy spar ( $\text{BaSO}_4$ ), orthorhombic, isomorphous with anhydrite; and the hydrous barium aluminum silicate, harmotome ( $\text{BaAl}_2\text{H}_2\text{Si}_3\text{O}_{15} \cdot 4\text{H}_2\text{O}$ ). Harmotome crystallizes in the monoclinic system and belongs to the class of zeolites.

There is no known commercial process for the recovery of the metal by chemical means. Barium chloride is electrolyzed in a cell with mercury cathode, forming an amalgam with 3 per cent barium, which is distilled at about 1000°C. to get the pure barium. The electrolysis is carried out at 100°C. As a metal it is used in some alloys with lead.

**Chief Alloys and Compounds.**—**Barium Acetate** ( $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ ).—White, flattened or monoclinic prisms, very easily soluble in water, insoluble in alcohol; the anhydrous salt is a white powder.

**Barium Carbonate** ( $\text{BaCO}_3$ ).—Colorless or white, rhombic crystals, or white amorphous powder, or soft white friable lumps; insoluble in water; slightly soluble in  $\text{NH}_4\text{Cl}$ . *Aq.*; soluble in  $\text{NH}_4\text{NO}_3$ . *Aq.* or  $\text{H}_2\text{CO}_3$ . *Aq.*; easily soluble in dilute  $\text{HCl}$ ,  $\text{HNO}_3$  or  $\text{HC}_2\text{H}_3\text{O}_2$ , with the evolution of  $\text{CO}_2$ ; melting point, 795°C.

**Barium Chlorate** ( $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ ).—Four-sided plates or colorless, monoclinic prisms or white powder, soluble in cold water, less in hot water, only slightly soluble in absolute alcohol; decomposes when heated, giving  $\text{O}_2$  at about 250°C., then a little  $\text{Cl}_2$ ; melts at about 400°C.

<sup>1</sup> U. S. Patent 1325043.

**Barium Chloride** ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ).—Colorless, flat, four-sided, monoclinic crystals or white powder, stable in air, with bitter, saline taste; soluble in water, slightly soluble in alcohol; when heated it loses its crystalline water without melting. The anhydrous salt melts at  $847^\circ\text{C}$ .

**Barium Chromate** ( $\text{BaCrO}_4$ ).—Heavy, yellow, crystalline powder or small rhombic crystals; insoluble in water; soluble in  $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{CrO}_4$ . *Aq.*; insoluble in  $\text{HC}_2\text{H}_3\text{O}_2$ ; used in yellow paint and Swedish matches.

**Barium Dioxide** ( $\text{BaO}_2$ ).—Coarse, heavy, grayish-white, amorphous powder, melting at full red heat, evolving  $\text{O}_2$ ; absorbs  $\text{CO}_2$  from the air, with the formation of  $\text{BaCO}_3$ ; insoluble in water; decomposed by boiling water; soluble in dilute acids, with the formation of  $\text{H}_2\text{O}_2$ .

**Barium Hydroxide** ( $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ).—White or colorless quadratic tablets, or white powder; absorbs  $\text{CO}_2$  from the air, forming  $\text{BaCO}_3$ ; somewhat soluble in water, with the formation of a colorless, alkaline solution called baryta water; considerably more soluble than  $\text{Sr}(\text{OH})_2$ ; slightly soluble in alcohol; readily soluble in cold  $\text{NH}_4\text{Cl}$ . *Aq.*; the hydrated crystal melts in its crystalline water at  $78.5^\circ\text{C}$ .; the amorphous form melts at red heat, and yields  $\text{BaO}$  and  $\text{H}_2\text{O}$  at higher temperatures.

**Barium Nitrate** ( $\text{Ba}(\text{NO}_3)_2$ ).—Colorless, transparent, lustrous, regular, octahedral crystals or white powder; somewhat hygroscopic; soluble in water; insoluble in concentrated  $\text{HNO}_3$ ; much less soluble in dilute  $\text{HNO}_3$  or  $\text{HCl}$  than in water, and still less soluble in dilute  $\text{HC}_2\text{H}_3\text{O}_2$ ; insoluble in absolute alcohol; solubility in dilute alcohol increases with the temperature; melting point,  $592^\circ\text{C}$ .; decomposes when heated. It is used in pyrotechnics and analysis.

**Barium Oxide** ( $\text{BaO}$ ).—Occasionally colorless, cubical crystals, generally grayish-white, porous, amorphous masses; combines with  $\text{O}_2$  at about  $450^\circ\text{C}$ . to form  $\text{BaO}_2$ , which is again reduced to  $\text{BaO}$  at higher temperatures. Takes up  $\text{H}_2\text{O}$  and  $\text{CO}_2$  on standing in air; soluble in water, with the evolution of heat to form an alkaline solution of  $\text{Ba}(\text{OH})_2$ ; easily soluble in dilute  $\text{HNO}_3$  or  $\text{HCl}$ ; soluble with combination in absolute alcohol; with acids it forms the corresponding salts; used in the glass industry.

**Barium Sulphate** ( $\text{BaSO}_4$ ).—Colorless, rhombic crystals when native; when precipitated it is a heavy, white, amorphous powder, insoluble in water,  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{HC}_2\text{H}_3\text{O}_2$ , and dilute  $\text{H}_2\text{SO}_4$ ; soluble in hot concentrated  $\text{H}_2\text{SO}_4$  or in fuming  $\text{H}_2\text{SO}_4$ ; soluble in  $\text{NH}_4\text{NO}_3$ . *Aq.*, very slightly soluble in  $\text{NH}_4\text{Cl}$ . *Aq.* It is used technically under the designations "blanc fixé" and "permanent white," as a water-color pigment for colored paper, and in wall paper as a size.

**Barium Sulphide** ( $\text{BaS}$ ).—White, yellowish, or reddish amorphous powder, soluble in water with decomposition; oxidizes in moist air; when exposed to sunlight and then placed in the dark, it gives off light. It is used for preparing As-free  $\text{H}_2\text{S}$ .

**Barium Alloys**.—Lead-barium alloys are made, and the components of the eutectic are pure lead and  $\text{Pb}_3\text{Ba}$ . This eutectic contains about 4.5 per cent barium and melts at  $282^\circ\text{C}$ .

## CHAPTER XXII

### ARSENIC

By WALTER C. SMITH<sup>1</sup>

**Arsenic** was not recognized as a metallic element until it was isolated by Schroeder in 1694; several of its compounds, however, were known from antiquity and were called arsenic. The name arsenic is used even today when the arsenious oxide is meant. Metallic arsenic is not used in the arts to a great extent, while the arsenious oxide (white arsenic of commerce) has many uses.

**Physical Properties.**—The metal has a steel-gray color and shows a brilliant luster on fresh fracture; it is known in both the crystalline and amorphous states. The crystalline form is very brittle. Other physical properties are: atomic weight, 74.96; number by Moseley's arrangement, 33; specific gravity (crystalline), 5.727, (amorphous), 4.71; fracture, coarsely crystalline; crystallization, hexagonal; melting point, red heat under pressure in the absence of oxygen; boiling point, volatile at 450°C. without melting; specific heat (crystalline) Sm, 0.083; (amorphous) Sm, 0.0758; latent heat of sublimation, 60 cal. per gram.

**Chemical Properties.**—Arsenic is not changed in dry air, but in moist air it loses its color and brilliancy and slowly changes into arsenious oxide. It burns with a bluish-white flame when heated in air, and gives off heavy white fumes of arsenious oxide, which have a characteristic odor resembling garlic.

Nitric acid oxidizes arsenic to arsenious oxide and then to arsenic oxide. *Aqua regia* yields a mixture of arsenious and arsenic compounds. Arsenic is soluble in hot concentrated sulphuric acid, but dilute acid does not attack it. Hydrochloric acid attacks it in the presence of air, feebly, to form arsenious chloride. It combines directly with chlorine to form arsenious chloride. It also combines directly with sulphur, when heated, to form arsenic sulphide. Metallic arsenic yields potassium arsenate when heated with niter or potassium chlorate.

In solution; silver will replace arsenic and *vice versa*, depending upon conditions, but neither Fe, Ni, Co, Cr, nor Mo will replace arsenic to a notable extent under any conditions. The single potential of arsenic (*vs.* calomel electrode = 0.577 volt) was found to be 0.55 in an  $\text{AsCl}_3$  solution of 1 g.-equivalent of arsenic per liter; and 0.54 volt in a corresponding solution of  $\text{AsI}_3$ .

**Uses.**—As already indicated, only limited quantities of metallic arsenic are used. A small amount of arsenic is added to lead in making lead shot, as it tends to prevent the formation of imperfect shot when the molten metal is dropped in the shot tower. A very small percentage of arsenic added to steel produces a metal which will take an extremely high polish. Arsenical copper is claimed to possess superior properties to pure copper for certain rolling and drawing operations.

The chief arsenic compound of commerce is the arsenious oxide ( $\text{As}_2\text{O}_3$ ), trioxide, or white arsenic. This is used in the manufacture of glass, in the textile and paint industries, and in the manufacture of weed killers, insecticides, and medicines.

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The boll weevil has in recent years wrought immense damage to the cotton crop of America. Investigations of the Department of Agriculture have developed a successful poison for this pest in calcium arsenate. The extensive use of this insecticide has increased the demand for white arsenic to such an extent as to cause a serious shortage.

At a meeting of the arsenic producers and consumers held in New York during December, 1922, to consider this question, some interesting data were brought out, as follows:

ESTIMATED CONSUMPTION FOR 1922, SHORT TONS OF  $\text{As}_2\text{O}_3$

Arsenate of lead .....	2,000
Paris green .....	1,200
Sheep dips .....	1,000
Wood killers .....	1,500
Glass .....	2,000
Proprietary mixtures .....	750
1922 consumption as calcium arsenate ..	4,000
Total 1922 consumption ...	<u>12,450</u>
1923 estimated consumption as calcium arsenate .....	12,000
Estimated arsenic consumption 1923 . . .	<u>20,450</u>
"Mineral Industry," 1921, gives:	TONS
Production for 1920 . . . . .	11,502
Imports .....	<u>3,740</u>
Total supply .....	<u>15,242</u>

The production for 1921 and 1922 was much less than this, because most of the copper smelters, which are the most important producers of  $\text{As}_2\text{O}_3$ , were either shut down or were operated at a curtailed rate.

The price of white arsenic has varied from  $1\frac{1}{2}$  to 20 cts. per pound during the last fifteen years. In 1922 the price ranged from 6 to 15 cts. per pound.

**Sources of Arsenic.**—Arsenic, while not abundant, is one of the most widely disseminated of all the metallic elements. It has been found in a number of places\* in the native state, usually associated with other metals. It occurs as mispickel or arsenopyrite, in many cobalt and cobalt-silver ores. Nearly all pyrite and sulphide ores of copper and lead contain more or less arsenic, and it is from these latter ores that the bulk of the American supply of arsenic is derived as a metallurgical by-product. The most important American producers of arsenic are listed as follows:

Company	Location	Source of arsenic
Am. Smelting & Ref. Co. ....	Denver, Colo.	By-product lead smelting
Am. Smelting & Ref. Co. ....	Tacoma, Wash.	By-product copper smelting
Am. Smelting & Ref. Co. ....	Perth Amboy, N. J.	By-product copper and lead smelting
Anaconda Copper Mining Co. ..	Anaconda, Mont.	By-product copper smelting
U. S. Smelting Co. ....	Midvale, Utah	By-product lead smelting
Jardine Mining Co. ....	Jardine, Mont.	By-product gold ore roasting

Metallic arsenic is produced by the sublimation of mispickel or leucopyrite in the absence of air, and by the reduction of arsenic trioxide with charcoal in cast-iron or steel retorts. The temperature and the pressure in the condensers have to be carefully controlled in order to yield the crystalline arsenic.

Previous to 1914 little or no metallic arsenic was made in the United States; about 50,000 lb. were imported annually, principally from Germany. The Hoskins Process Development Co.<sup>1</sup> of Chicago, Ill., began the manufacture of metallic arsenic in order to supply the American market after the German supply had been cut off by the war. The arsenic of 99.5 per cent grade is made by the reduction of commercial arsenic trioxide with charcoal in a battery of four gas-fired furnaces as shown. Three of the furnaces take a charge of about 200 lb. each and the fourth furnace holds 450 lb. of charge.

The charge is mixed in a rotary mixer in the proportions of 1 lb. of charcoal to 4 lb. of arsenic trioxide. The capacity of the plant is from 250 to 300 lb. per day, or not less than 4,000 lb. of metallic arsenic per month.



FIG. 1.—Arsenic furnaces, with condensers in background.

The furnaces are built of steel pipe, surrounded by fire brick, enclosed in a steel jacket and supported on a pipe frame. The charging end of the retorts is sealed with a clay gasket in which is embedded a  $\frac{1}{4}$ -in. copper water pipe. The cooled surface condenses arsenic vapor and seals any leaks in the clay gasket. At the back of and attached to the retort is a water-cooled condenser, which is vented by means of a water seal so as to allow the escape of the uncondensed gases. Figure 2 shows the left side of one of the furnaces. Two condensers are shown in the background of Fig. 1.

The period of operation for the large furnace is about 10 hr., and for the smaller furnaces 7 hr. The gas is then shut off, and the retort and the condenser are allowed to cool before the condenser is opened for the removal of the metallic arsenic. Figure 3 shows the discharge end of one of the furnaces. The metallic arsenic is removed from the condenser with a bar and hammer, and is then ready for packing and shipment.

<sup>1</sup> JONES, C. H., *Chem. Met. Eng.*, Nov. 17, 1920.

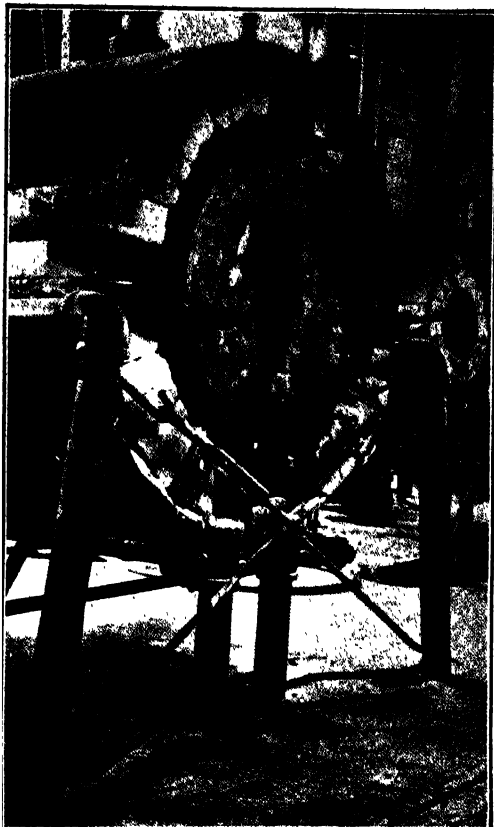


FIG. 2.—Side of arsenic furnace.

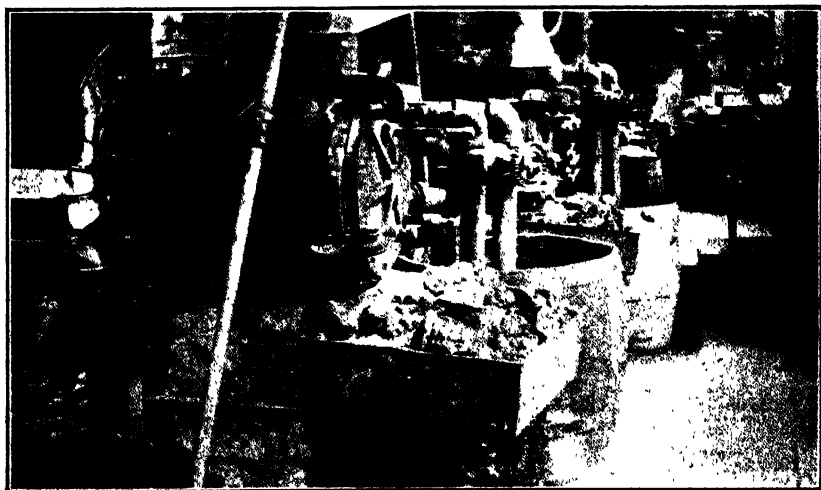


FIG. 3.—Discharge end of furnaces.



**Production of White Arsenic.**—The production of white arsenic is generally carried out in two stages: the production of a crude white arsenic, followed by a refining of this crude material. When arsenic-bearing materials, in which the arsenic exists in the reduced state, are roasted, the arsenic is volatilized and passes off with the gaseous products. Arsenic trioxide begins to condense at  $218^{\circ}\text{C}.$ , hence the flue products caught in the cooler parts of the flue system carry considerable arsenic. More or less dust carried by the gases and other volatile materials can contaminate the arsenic trioxide, and these are removed in the refining operations.

The roasting operations may be carried out in muffle, reverberatory, or one of the various types of roasting furnaces; coke, gas, or oil is used for fuel in reverberatory or roasting furnaces in order to reduce the danger of contamination of the product with soot. The crude arsenic trioxide is collected in cooling flues, bag houses, or by Cottrell precipitators.

**Crude White Arsenic from Metallurgical Products.**—The arsenic carried by lead and copper ores is concentrated during the roasting and smelting operations in the flue products, which are caught in the cooler parts of the flue system. Lead bag-house dust, carrying 30 per cent arsenic, and copper furnace and roaster dusts, carrying 20 to 30 per cent arsenic, are not uncommon. The arsenic in these dusts exists largely in the form of the trioxide ( $\text{As}_2\text{O}_3$ ).

At one of the American plants the bag-house dust, carrying about 30 per cent arsenic, is mixed with a small quantity of fine pyrite or low-grade lead sulphide concentrates and is fed to the hearth of a Brunton roasting furnace. The pyrite is added to the dust in order to prevent the formation of non-volatile arsenites in the residue from the roast, and it also gives a clinkered residue which makes a suitable blast-furnace feed. The Brunton furnace volatilizes from 75 to 90 per cent of the arsenic in the dust which is charged to it. The gases from the Brunton furnaces pass through a cooling flue built in the form of a number of connecting rooms or chambers. Brick is usually employed in the construction of these chambers, or kitchens, as they are called. The temperature of the gas in the cooling flue is so regulated that it enters the first kitchen at approximately  $220^{\circ}\text{C}.$ , and by the time it reaches the last kitchen it has dropped to  $100^{\circ}\text{C}.$ , or less. The crude arsenic trioxide collects in the kitchens and is removed at the end of the campaign for refining. This crude arsenic trioxide should contain from 90 to 95 per cent  $\text{As}_2\text{O}_3$ .

The crude  $\text{As}_2\text{O}_3$  is resublimed in order to remove impurities; this operation is repeated until the desired purity is obtained. Reverberatory furnaces are used for this work and are fired with gas or coke. The furnace gases pass through settling chambers and then to the kitchens, where the refined arsenic trioxide is collected. The product should contain over 99 per cent  $\text{As}_2\text{O}_3$ .

**Arsenic Production at Anaconda.**<sup>1</sup>—The main source of arsenic at Anaconda is the Butte copper ores. The concentrates from these ores average 1.6 per cent  $\text{As}_2\text{O}_3$ . In the roasters the arsenic is reduced to 0.25 per cent in the calcined product, and in the smelting operations a part of the arsenic in the calcines is volatilized and passes into the flue system.

The combined gases from all furnace operations pass through 2,500 ft. of flue system, and are then treated in the Cottrell precipitators before passing to the main stack for discharge to the atmosphere. The arsenical dusts from the main flue and

from the Cottrell treaters are smelted in a large reverberatory furnace located near the base of the stack, thereby volatilizing most of the arsenic and recovering the copper, silver, and gold in the form of matte. The gases from this furnace pass into a culvert at a temperature of approximately 1000°C. and are sprayed with water to

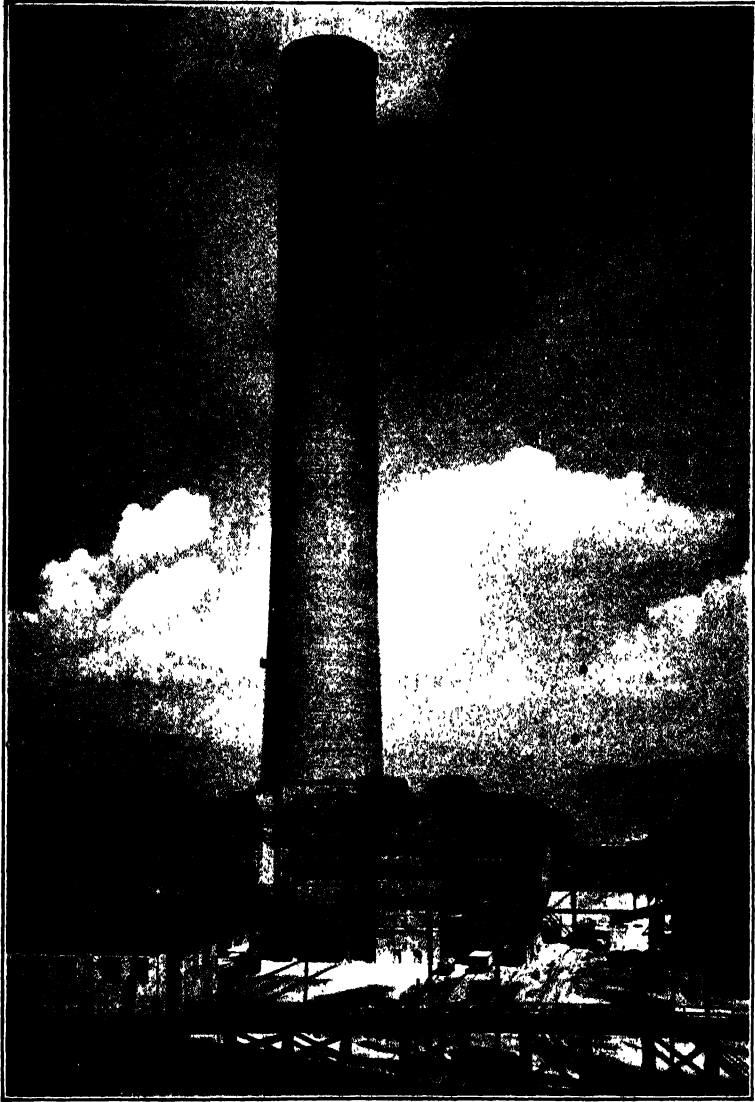


FIG. 4.—Cottrell treaters and main stack, Anaconda Copper Mining Co.

cool and humidify the gases. The cooled gases then pass to the first of two sets of Cottrell treaters (hot treaters), and then to the second set (cold treaters). The hot treaters collect about 28 per cent of the arsenic charged to the reverberatory as a product assaying 70 to 75 per cent  $\text{As}_2\text{O}_3$  and 0.2 per cent moisture; the cold treaters

catch about 17 per cent of the arsenic charged to the reverberatory as a dust assaying 80 to 85 per cent  $\text{As}_2\text{O}_3$  and 0.5 per cent moisture; and about 18 per cent more of the arsenic charged to the reverberatory is removed from the flue system as high-grade arsenic dust. The balance of the arsenic charged to the reverberatory furnace passes off in the slag and matte. Some of the flue cleanings carry 30 to 50 per cent  $\text{As}_2\text{O}_3$ , and are quite damp. These are stock piled for drying and then recharged to the reverberatory furnace.

The arsenical dusts from the hot and cold treaters and the high-grade flue dust are sent to the arsenic roasters. When these dusts are treated in the refining furnace it is necessary to make two refinings in order to secure a soluble white arsenic for market purposes. It has been found cheaper to give these dusts a treatment in the arsenic roasters and then one refining.

**Arsenic-roasting Plant.**—Three rows of McDougall roasters in the roaster building were remodeled into three sets of arsenic-roasting furnaces. A set consists of four 16-ft. six-hearth furnaces connected in series for the gas flow. The first, or roasting, furnace has two fire boxes, on the third and fifth hearths

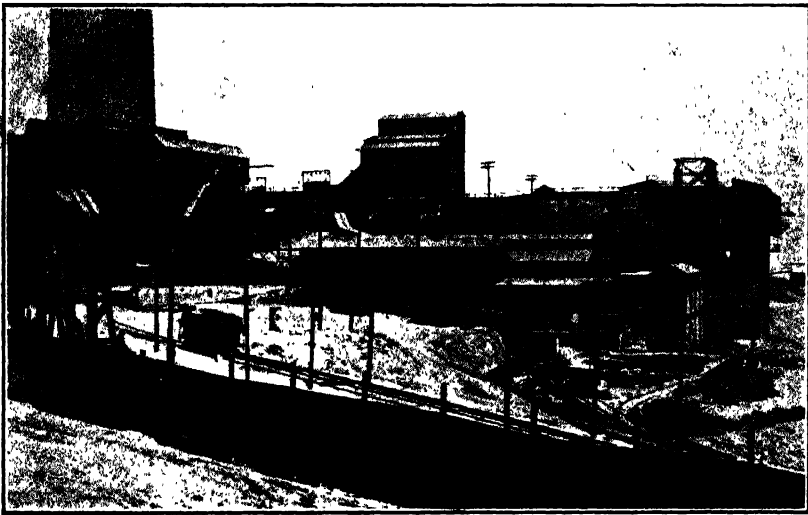


FIG. 5.—Reverberatory stack and hot and cold treaters.

respectively, and is equipped with a special apron feeder for charging the dust. The other three furnaces in each set serve as the condensing chambers. The inside hearths have all been removed and a center vertical partition installed. This partition has an opening at the bottom to permit the passage of the gas. The gas enters each condenser at the top, passes down one side of the partition and up the other side, leaving at the top to enter the top of the next condenser. After leaving the last condenser the gas passes into the main dust chambers and flue system. The bottom sets of arms are left in each of the condensers and are operated periodically to remove the collected arsenic, which is then sent to the refining furnaces.

The roasting furnaces are operated at a temperature of approximately  $650^{\circ}\text{C}$ ., as higher temperatures cause fusion of the condensed arsenic in the condensers. Experiment has proved that 50 per cent  $\text{As}_2\text{O}_3$  is the maximum permissible in the feed to the roasters if a fusion of the material in the roasters is to be prevented; the high arsenical dusts, therefore, are diluted with a very fine flue dust. Copper concentrates and limestone were tried, but did not prove satisfactory. It was found that better results were obtained when coal to the amount of 10 per cent of the weight of the arsenic dust was mixed with the roaster feed.

The roasters yield a residue, carrying about 15 per cent  $\text{As}_2\text{O}_3$ , which is sent to the main copper reverberatory furnaces for treatment. The crude arsenic trioxide removed from the condensers assays about 90 per cent  $\text{As}_2\text{O}_3$ .

The maximum capacity of a roasting furnace is 30 tons of charge per 24 hr., but 20 tons of charge per day give the most efficient operation consistent with the cost. A smaller tonnage per furnace-day would volatilize a greater percentage of the arsenic out of the charge, but the increased cost could not be justified.

**Refining Plant.**—Two refining furnaces of the reverberatory type have been installed. Each furnace has an overall length of  $36\frac{1}{2}$  ft., and a width of 14 ft.; the hearths are  $26\frac{3}{4}$  ft. long and 12 ft. wide. The main hearths are made of

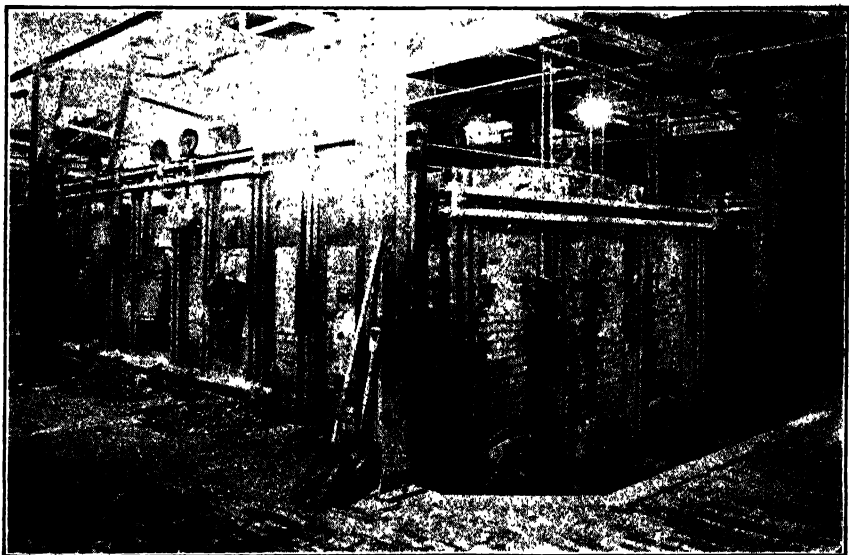


FIG. 6.—Arsenic refining furnace.

cast-iron plates. Two fire boxes are used, one at the back of the furnace, whose hot gases pass under the cast-iron hearth and back over its top, and the other at the front of the furnace, whose gases pass only over the hearth.

The charge consists of 8 tons per furnace-day of the 90 per cent  $\text{As}_2\text{O}_3$  crude arsenic from the arsenic roasters. The charge is dropped to the hearth through openings in the roof, and is spread out with rabbles; part of the charge is dropped during the afternoon shift and the balance during the night shift. A thin layer of crushed rock is spread over the hearth before charging the furnaces to facilitate the removal of the residue after the arsenic has been volatilized. A special crew cleans the hearths on the day shift. Each refining furnace will treat 30 tons per day, when treating very

high-grade dust or when rerefining. High-grade material is dropped on all three shifts and the residue is removed once in two or three days. A temperature of  $550^{\circ}\text{C}$ . has been found to give the best results in these furnaces. A draft of 0.05 in. of water gives satisfactory results. The volatilization of about 80 per cent of the arsenic in the 90 per cent  $\text{As}_2\text{O}_3$  material fed to the furnace gives the most economical operation. The refining-furnace residues are smelted in the stack reverberatory.

**Condensing Kitchens.**—Three sets of chambers are used for handling the gases from two refining furnaces, two of these chambers being used while the third is being cleaned. Each chamber is approximately 225 ft. long and is divided into thirty-nine kitchens. The kitchen nearest to the furnace is larger than the others and is used for settling the non-arsenical dust. Its temperature is about  $295^{\circ}\text{C}$ ., or above the condensation temperature of  $\text{As}_2\text{O}_3$ . The gases cool as they pass through the kitchens by radiation and leakage, and leave the system at from 90 to  $100^{\circ}\text{C}$ . Most of the arsenic settles out in those kitchens which have tem-



FIG. 7.—Arsenic barreling plant.

peratures from  $180$  to  $120^{\circ}\text{C}$ . The kitchens nearest to the furnace contain a fused or amorphous arsenic, black in color, and carrying about 95 per cent  $\text{As}_2\text{O}_3$ . This material is rerefined. The material in the succeeding kitchens increases in arsenic content to 99.9 per cent  $\text{As}_2\text{O}_3$ , and is white and crystalline. The grade of the dust diminishes in the last kitchens, and changes to a fine white powder.

**Bag House.**—The gas leaving the last kitchen contains a very fine arsenic dust which will not settle in the kitchens, and this dust is caught in a bag house. The two refining furnaces deliver approximately 18,000 cu. ft. of gas per minute at the outlet to the last kitchens. This gas is forced through the bags by a No. 11 Sirocco fan. The bag house contains two sections of 100 bags each; the bags are 30 ft. long, 18 in. in diameter and are made of wool. The bags are shaken once a shift, the dust falling into hoppers, from which it is drawn. The bag-house product assays about 90 per cent  $\text{As}_2\text{O}_3$ , and is sold as crude arsenic or is rerefined. The life of the woolen bags is satisfactory except when materials carrying too much acid are treated in the refining furnaces.

**Packing.**—At the end of each refining campaign the kitchens are sampled, and the samples are run for total arsenic and soluble arsenic. The product is then graded and packed in barrels of 500 lb. each; it is made into 50,000-lb. lots and sold as white soluble, white insoluble, or crude arsenic. The capacity of the packing room is 18 tons per 8-hr. day. The white insoluble arsenic can be changed to the white soluble by rerefining if market conditions demand.

**Manufacture of White Arsenic by the Jardine Mining Co.**<sup>1</sup>—The Jardine Mining Co., at Jardine, Mont., treats a low-grade gold ore containing arsenopyrite in the following manner: The ore, carrying about \$7.50 in gold per ton and 5 per cent arsenic, is first concentrated, yielding a concentrate assaying 2 to 3 oz. in gold per ton and 38 per cent arsenic. The concentrate is then treated in a reverberatory-type roaster fired with soft coal, and the arsenic trioxide is collected from the gases in a series of chambers or kitchens. The waste gases are sent to a stack, the top of which is 250 ft. higher than the furnace. The arsenic trioxide produced from the concentrates is not white; it is, therefore, stored until enough has been accumulated for refining. It is then refined in the same furnace, except that a coke fire is used instead of a coal fire. The calcined concentrates are shipped to the smelter. The capacity of the arsenic plant is 100 tons of oxide per month. The mill is treating approximately 150 tons of ore per day, and the yield of arsenic is about 57 to 65 per cent.

**Manufacture of Arsenic Trioxide from Arsenical Pyrite.**<sup>2</sup>—The arsenical pyrite is crushed by jaw crushers and is then ground in ball mills. The ground product is washed to remove as much foreign matter as possible, and dried. The drying was formerly done on the top of the roasting furnace, but this method cools the furnace and reduces the roasting efficiency. At present the drying is done in a mechanical drier, which is equipped with a screw conveyor for stirring and progressing the charge.

The dried concentrate is charged to the top of a roasting furnace of the MacDougall type, 18 to 30 ft. high and 10 to 16 ft. in diameter. The rabble arms rotate at a speed of 5 r.p.m., but even at this speed some dust is carried out of the roaster with the gases, and this dust must be separated from the gases before they pass to the condensing chambers. This is done by a dust separator placed at the gas outlet of the roasting furnace. This separator consists of an insulated chamber containing two rotating screens of fine mesh provided with revolving brushes for cleaning. This arrangement removes nearly all of the solid matter in the gases and offers but little resistance to the flow of the gases. The cleaned gases are then drawn by a fan through the condensing chambers.

The condensing chambers are made of sheet lead and are divided into a number of smaller compartments by sheet-lead baffles which increase the condensing surface. Water sprays are introduced into the chambers to facilitate the condensation of the arsenic trioxide and to flush the condensed material out of the chambers into a collecting tank. Lead is the only metal which will withstand the action of the sulphurous acid generated from the sulphur in the concentrate.

The mixture of water and arsenic trioxide is then filtered in vacuum filter tanks and the moisture content is reduced to 20 to 25 per cent by the addition of some dry arsenic trioxide. It is then passed through a rotary drier, which is lined with porcelain to prevent sticking to the sides of the drier. The drying temperature employed is about 180°C., in order to prevent the loss of arsenic by sublimation during drying.

The crude arsenic trioxide is refined by sublimation. Furnaces 10 to 14 ft. in diameter, equipped with cast-iron hearths and rotating rabblies, are used for this operation. The crude arsenic trioxide is charged to the furnaces through openings in the roof. The proper temperature has been found to be 245°C. Approximately 70 parts of fuel are required for each 100 parts of refined arsenic trioxide.

The final condensation takes place in lead-lined wooden chambers containing baffles and placed over a trough which carries a porcelain screw conveyor for the removal of the collected material. About 0.65 lb. of arsenic trioxide is condensed per square foot of condensing surface. The exit gases from the condensing chambers pass to a coke-filled scrubber, where the last of the arsenic is removed with water sprays. The finished product is finely powdered, perfectly white, and will assay 99.0 per cent  $As_2O_3$ .

R. W. Bridges<sup>1</sup> gives the method used for the recovery of arsenic from the cobalt ores of Cobalt, Ont. The ores are crushed and then ground so as to pass 30 mesh in ball mills. The charge, with the proper fluxes, is smelted in 32- by 72-in. blast furnaces of capacities of 25 to 30 tons per day. The fluxes used are limestone and a low-grade siliceous ore. The products are: flue dust and crude arsenic trioxide, slag, silver bullion, and speiss. The flue dust and crude arsenic trioxide are caught in suitable settling and condensing chambers. The flue dust is returned to the blast furnaces and the crude arsenic trioxide is sent to the arsenic refinery for retreatment. The slag is discarded if it carries less than 10 oz. of silver per ton. The silver bullion assays about 860 fine and is treated in a cupel furnace for 24 hr., after which treatment it averages 994 fine. The speiss—a typical assay of which is Ag, 1,480 oz.; As, 31.3; Co, 25.2; Ni, 15.3; Fe, 16.1 per cent—is crushed, ground, mixed with 20 per cent of NaCl and roasted in Edwards mechanical roasters having a daily capacity per furnace of 2,400 lb. The roasted product is then leached with cold water to remove the undecomposed NaCl and soluble salts of cobalt, nickel, and copper, which have formed in the roasting operation. The residue is then leached with four successive batches of  $Na_2S_2O_3$  solution to remove the silver. The cobalt, nickel, and copper are recovered from the water leach liquors and the leached residues. The crude arsenic trioxide is resublimed in the arsenic refining furnaces in the usual manner, producing an arsenic trioxide of 99.0 per cent.

**Manufacture of Lead Arsenate.**—A number of methods have been proposed for the manufacture of lead arsenate, the first step of which is the conversion of arsenic trioxide or a soluble arsenite into arsenic acid or a soluble arsenate. A fusion of arsenic trioxide with caustic soda or sodium carbonate and sodium nitrate yields sodium arsenate, which is then dissolved in water and mixed with the solution of a soluble lead salt, as the nitrate or acetate, the insoluble lead arsenate being precipitated. Chlorine gas will slowly convert a solution of sodium arsenite into sodium arsenate; it will also convert a mixture of arsenic trioxide and water into arsenic acid. Nitric acid and arsenic trioxide react violently to form arsenic acid; the gaseous products of the reaction contain considerable nitric acid and are generally sent to a condensing system for the recovery of this acid.

A patent<sup>2</sup> issued to Luther and Volck covers the formation of lead arsenate by roasting the combining parts in the presence of oxygen. Lead arsenite is formed and oxidized to lead arsenate by roasting in the presence of oxygen. The lead arsenite is produced by heating white arsenic with lead or lead oxide. It may also be formed as a mixture of lead arsenite and lead arsenate by heating red lead with white arsenic.

<sup>1</sup> "Metallurgy of Cobalt, Ontario, Ores," *Can. Mining J.*, Jan. 15, 1916.

<sup>2</sup> U. S. patent 929962, Aug. 3, 1909.

Lead arsenate may be formed directly by roasting white arsenic with lead peroxide or lead nitrate or one of the lower oxides of lead with an oxidizing agent.

The Barstow and Cavanagh patent<sup>1</sup> consists in combining litharge with arsenic acid assisted by the action of a catalytic agent; the direct combination of arsenic acid and litharge is too slow to be of commercial value. The catalytic agent used is a small amount of either nitric or acetic acids.

U. S. patent 1398267, issued to John Kirby, Matthew S. Hopkins, and Charles B. Bernhart, of Reading Pa., covers the use of sulphonic acids of the aromatic hydrocarbons as catalytic agents for the manufacture of lead arsenate from litharge and arsenic acid. The purity of the sulphonic acid used is non-essential, as the mixture of sulphonic acids obtained by the sulphonation of the commercial grades of hydrocarbons will act effectively. The lead arsenate produced by the use of these reagents possesses the physical requirements important for an insecticide, namely, large bulk, good dispersion, proper adherence to the foliage treated, and effective insecticidal properties.

The preparation of the catalyst is carried on approximately as follows: A commercial grade of a suitable hydrocarbon, such as ordinary naphthalene, is sulphonated in the usual manner, the excess sulphuric acid is removed by precipitation with a soluble lead salt, and the clear liquor is separated by decantation or filtration.

A charge of 700 lb. of litharge is placed in a tank and agitated to keep the litharge in suspension in water. About 50 lb. of the mixed sulphonic acids is added, the quantity to be used depending upon the speed of reaction required and the physical properties desired in the product. Approximately 600 lb. of a 75 per cent arsenic acid is then slowly added. The temperature is raised to 160°F. The mass slowly changes in color to white as the litharge is converted to lead arsenate. Any excess of litharge is removed by the addition of more arsenic acid. The resulting mass of lead arsenate, the lead salt of the sulphonic acid, and water may be washed and the lead arsenate pressed for use as paste or as powder after drying and grinding. The sulphonic acid liberated by the precipitation of the lead arsenate is available for further use as a catalyst.

Lead carbonate or basic lead carbonate can be substituted for litharge and a solution of a soluble arsenate for the arsenic acid.

**Manufacture of Calcium Arsenate.**—Calcium arsenate is manufactured by the method developed by the U. S. Department of Agriculture at Tallulah, La. This consists in the oxidation of arsenic trioxide to arsenic acid by means of nitric acid. The arsenic acid is then neutralized with sodium hydrate to form sodium arsenate, and calcium arsenate is precipitated by the addition of milk of lime to the solution of sodium arsenate. The calcium arsenate produced must have the necessary physical properties for use as an insecticide.

**Precautions in Handling Arsenic Trioxide.**—Arsenic trioxide is very poisonous and considerable care must be exercised to prevent occupational poisoning. Ample draft in the furnaces and flue systems, proper ventilation in all parts of the arsenic plant, proper bathing facilities for the men, and the use of efficient respirators have greatly reduced the danger of arsenic poisoning. One American plant has successfully applied the pneumatic system to the removal of the arsenic trioxide from the kitchens.

<sup>1</sup> U. S. patent 1228516, May 5, 1917



## CHAPTER XXIII

### ANTIMONY

By G. C. RIDDELL<sup>1</sup>

**Nature and Uses.**—Metallic antimony unalloyed has few industrial uses. It is a brittle metal, of silvery luster, easily powdered, of rather low melting point (630°C.), and of specific gravity about 6.5. Antimony alloys readily with most of the heavy metals, the alloy being harder than the pure metals, and in most cases possessing the property of prompt expansion on solidifying, which enables very sharp impressions to be obtained in casting. The alloys with lead and tin are by far the most important, and type metal, bearing metals, britannia metal and hard metal (antimonial lead) are the commodities consuming the largest amount of antimony.

Type metal is an alloy of antimony, lead, and tin; bearing metal (babbitt, or anti-friction metal) an alloy of antimony, tin, and copper; britannia metal ("white metal") an alloy of antimony, tin, and copper, with some zinc, and, rarely, small quantities of other metals. Antimony alloys are used to a small extent in battery plates, toys, and cable coverings. Lead-antimony alloy or hard lead is used in making acid-resisting valves.

It is a highly important war metal, being used especially in shrapnel, for bullets, in primers, and to produce a white smoke for range finding. Antimony compounds are widely used in medicine. The well-known tartar emetic and antimony fluoride are employed as mordants, in the dyeing of cloth. The sulphide is an important ingredient in safety matches, being placed as a compound on the match box, or striking surface, and on the head of the match. The precipitated sulphides of antimony are used in vulcanizing, and as color pigments in the paint trade, and the pure sublimed tetroxide is a common ingredient in enamels for coating metal ware. The trioxide is used in the manufacture of glass. Antimony oxides meet the high standards required for paint and enamel manufacture and are growing in importance as white pigments.

Patents have been recently issued on new antimony chemical products that may considerably extend the industrial usefulness of the metal. These products—solutions of antimony trichloride in benzol, and creosote—will go into the building and paper trades as fire preventives, and into the lumber trade as wood preservatives.

**History.**—In point of use by man, antimony is one of the oldest of the metals. The natural sulphide was known to the people of ancient times. It was used by them as medicine, and as an article of toilet for eyebrow painting by women of biblical times. A vase found at Tello, Chaldea, cast in metallic antimony, discloses the reduction of the metal itself by the ancients.

Basil Valentine, a German monk of the fifteenth century, and Agricola,<sup>2</sup> wrote of liquation, precipitation, and starring of regulus. Valentine gave distinct recipes for

<sup>1</sup> 1 Broadway, New York, N. Y.

<sup>2</sup> "De Re Metallica," Vol. 12, 1557.

the preparation of antimony trichloride, basic chloride, trioxide, and potassium antimonate. In the fifteenth century, antimony was in use for printers' type, and in mirrors and bells. In the sixteenth century came its use as a medicine. Of the methods now obtaining in antimony metallurgy the precipitation of metal from sulphide by iron appears in writings of the seventeenth century (Ercker), and, in the eighteenth century, the roast-reduction procedure came into use. In the early nineteenth century came the reverberatory furnace, and in 1896, electrolytic antimony first appeared in the market.

**Allotropic Forms.**—Like phosphorus and arsenic, antimony has several allotropic forms, some of them with unique characteristics. Besides the gray form of antimony, the best-known and most common, there is another form, in which metallic antimony has the property of exploding. The latter form is unstable, and changes readily to the stable metallic form.

*Metallic antimony*, pure, is silver-white with a bluish tinge, shiny and brittle, crystallizing in the hexagonal system. When cooled slowly from the molten state, under a cover of slag, the solidified surface takes on a fern-like appearance—the "antimony star," which has become a feature of the commercial refining of the metal.

*Explosive antimony*, already referred to, is metallic, but distinctly different from the ordinary form of the metal. It is an uncommon form of antimony, and can be produced by electrolysis from a solution in chlorine and bromine. Also, in a bath of hydrochloric acid and antimony protochloride, with antimony metal as anode and platinum as cathode, explosive antimony is deposited on the platinum. This antimony, rubbed in a mortar, strongly detonates, giving off light and heat. It will explode, also, if scratched with a sharp point, giving off heat and setting free a white fume. The same phenomenon can be produced by heating the dried cathode deposit to 200°C., the resulting reaction product being the ordinary antimony.

*Black antimony* is another metastable amorphous form, produced when antimony metal vapor is suddenly cooled. This form of the element is more active, chemically, than the ordinary metallic form, being sometimes spontaneously combustible. At 100°C. it changes gradually to the ordinary metal; at 400°C. the change is sudden.

*Yellow antimony*, the most unstable of the several forms of antimony, is without any metallic property, and corresponds to white phosphorus and yellow arsenic. This form, obtained by introducing oxygen into antimony hydride at -90°C., is of academic interest only. It changes into black antimony above -90°C., under ordinary light.

**Chemical Properties.**—Antimony has three valences, 3, 4, and 5. Its chemical properties resemble those of arsenic, and it stands close to the zinc group, being closely similar to germanium. Analytically, antimony presents some difficulty in its separation from zinc and tin. Antimony is but slightly oxidized at ordinary temperatures. On heating, however, the metal readily oxidizes to the trioxide. The metal is also readily oxidized by any oxides which can easily give up their oxygen component, such as lead oxide and manganese peroxide. It also oxidizes in the presence of steam.

In acids, the metal is unattacked by dilute sulphuric acid, but forms antimonious sulphate in hot, concentrated sulphuric acid. It is attacked by hydrochloric only when in a state of fine powder. In concentrated nitric, it is converted to the trioxide. In *aqua regia* it dissolves easily to the pentachloride.

Mixed with niter and soda, antimony explodes on ignition. With alkaline nitrate and chlorate, the metal decrepitates, forming an antimoniate.

## COMMERCIAL COMPOUNDS

**Pigments.**—1. "Antimony white" is the trioxide of antimony which is formed as a very fine powder in the flues and dust chambers of antimony-roasting furnaces. It can be collected in this form and used without further treatment for certain paint purposes, but a specially ground and prepared oxide called Timonox, is produced in England, of superior texture, opacity, and whiteness, which has become of great usefulness among pigments.

2. "Antimony black" is metallic antimony deposited electrically or chemically as a fine powder from an antimony solution, and is used as a bronzing pigment for metals and plaster casts.

3. "Antimony vermilion," a red trisulphide of antimony, may be formed by precipitating an antimony salt from solution with sulphureted hydrogen. As a pigment, it is in many ways superior to red oxide of lead, red chromate of lead, or mercury vermilion.

4. "Antimony yellow" is produced by the slow oxidation of the sulphide; various shades of yellow are formed by mixing it with red lead and zinc white.

5. "Antimony blue," "antimony violet," etc. are other pigments produced by mixtures of the foregoing with other mineral compounds.

**Rubber Vulcanizing and Filling.**—The red trisulphide of antimony is fused with sulphur and thus converted into pentasulphide, the product being dissolved in a solution of sodium sulphide. The pentasulphide crystallizes out as a red powder when the solution is evaporated, and in the vulcanizing process this powder parts with the excess of sulphur and is reduced again to the trisulphide. The latter mixes mechanically with the rubber, giving a red color.

**Enameling.**—In enameling processes and in glass staining antimony tetroxide is mixed with white lead and borax to produce a yellow color. A white enamel is now made with the trioxide, this compound, to some extent, replacing tin oxide.

**Shrapnel.**—Reference has already been made to the use of antimony in shrapnel bullets, and antimony sulphide has also been used to form part of the powder composition for shrapnel shells, when it is desired to produce a dense cloud of white smoke on bursting.

**Matches.**—Antimony trisulphide is used in making safety (Swedish) and wax matches, as well as in the composition on the side of the box on which the matches are ignited. The heads of the matches contain about 3 per cent of the trisulphide, while the composition of the box contains about 8 per cent of the same material. Antimony crude is used by the match manufacturers.

**The Metallurgy of Antimony.**<sup>1</sup>—Stibnite ( $\text{Sb}_2\text{S}_3$ ), antimony sulphide or glance, is the chief ore from which antimony is extracted. The major deposits of the world—China, Mexico, Bolivia, France—are mainly stibnite. The other ores—cervantite, kermesite, valentinite, senarmontite, which occur only in small quantities in nature—together with the fumes and slags from the previous smelting of antimony are generally mixed with the stibnite before smelting.

Dry methods have, up to the present time, proved most successful, and are generally adopted. Wet processes and electrometallurgical methods have had much attention in America and France, but have not yet found practical application. The

<sup>1</sup> The metallurgical works of Schnabel, Kerl, C. Y. Wang, and K. C. Li, have been freely used in the compilation of this chapter.

electrolytic production of metal from antimony ore is feasible, and offers attractive possibilities.

The more or less pure sulphide of antimony is called "needle," liquated, or "crude" antimony, and the refined metal itself is called antimony "regulus." This use of the term "regulus" for designating antimony metal is a bit peculiar, and somewhat confusing, but the term is securely fixed in the trade. Ordinarily, a regulus is a matte, or sulphide, of a metal, but as used from ancient times in connection with antimony, it has indicated the pure metal and not the sulphide or crude. The ancients gave the name "regulus" to metallic antimony because of a peculiar action it has upon the working properties of the king of metals—gold. One part of antimony in one thousand parts of gold destroys the working properties of the gold—thence the name "regulus," or "little king."

A blocking out of the metallurgy of antimony results in the following skeleton of processes.<sup>1</sup>

#### EXTRACTION OF METALLIC ANTIMONY FROM ORE

##### I. By dry methods:

##### A. Preparation of products for the production of metallic antimony:

##### 1. Liquation of crude antimony:

##### a. Intermittent working:

(1) In pots in open fire

(2) In pots in furnace:

(a) Receiver placed outside the furnace.

(b) Receiver placed below pot in furnace.

##### b. Continuous working.

(1) In tubes

(2) In reverberatory furnaces

##### 2. Preparation of the stable tetroxide:

##### a. Rabble furnaces

##### b. Hand furnaces (long-bedded).

##### 3. Preparation of the volatile trioxide:

##### a. Herreshmidt process

##### b. Chatillon process.

##### c. Plews process.

##### d. Italian—Miniere e Fonderie d'Antimonio Società Anonima's process.

##### B. Methods for the production of metallic antimony:

##### 1. Reduction of the oxide (either tetro or tri):

##### a. In reverberatory furnaces

##### b. In water-jacket or blast furnaces

##### c. In crucibles.

##### 2. Extraction of metal from crude:

##### a. English precipitation method

##### 3. Direct processes (metal directly extracted from the ore):

##### a. Reverberatory bath furnaces.

##### b. Water-jacket or blast furnaces

##### c. Converters.

##### II. By wet methods.

##### III. By electrolytic methods.

#### REFINING OF ANTIMONY METAL

##### I. In pots.

##### II. In reverberatory furnaces.

<sup>1</sup> After WANG, C. Y., "Antimony, Its Chemistry, Metallurgy, Uses."

## EXTRACTION OF METALLIC ANTIMONY

**Liquation of Crude Antimony.**—The first step in the smelting of antimony is a simple one—the process of “liquation,” which produces crude or needle antimony. Ores containing 90 per cent and more of the sulphide are rated, without treatment, as crude antimony. Ores carrying less than 60 and more than 45 per cent sulphide are brought into the crude form by the liquation process, which is merely the subjection of the ore to a proper temperature—just at or below red heat—until 85 to 88 per cent of the sulphide content fuses and runs out of the ore into pots set for catching it.

Ores to be liquated are broken to about walnut size. If the pieces be larger than this, the low heat used will not penetrate effectively, and if the size be smaller than walnut the ore tends to pack too closely and the same thing occurs. A packed charge also prevents the free escape of the fused sulphide. Pieces of smaller size, and all ores containing less than 40 per cent of sulphide, are used for producing regulus by the roasting and reduction methods, without liquation. The temperature of liquation is carefully maintained at the proper range. Any increase above a red heat results in volatilization of the sulphide, and if the temperature runs too low, too much sulphide remains in the residues.

In China the smelting (or liquation) of ore into crude is done in pots, which are either heated directly by contact with the fuel in the furnace, or by the flame only. In pot liquation, the working is intermittent, but a continuous process is also in use employing tubes, or reverberatory furnaces, in which there is economy of fuel. Liquation is thus carried out either by: (1) Intermittent working in pots; or (2) continuous working in tube furnaces or reverberatories.

**Intermittent pot liquation** is primitive and simple, and can be performed readily at the mine. If ores are rich and fuel accessible, it is a very satisfactory

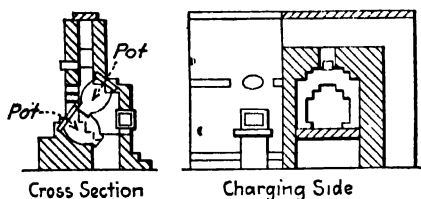


FIG. 1.—Liquation furnace and pots used in China.

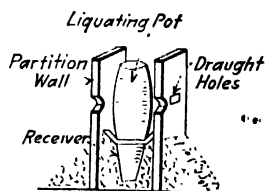


FIG. 2.—Open-fire liquation in the Harz.

method. In China the liquation is carried out in a narrow brick furnace containing two pairs of pots. One pot sits above the other, and properly sized ore is charged into the upper pot. Heat liquates out the sulphide, which trickles through the  $\frac{1}{2}$ -in. holes in the base of the charge-pot into the lower or collecting pot. When sufficient molten sulphide, or crude, has accumulated in the lower pot it is ladled out into molds. The collecting-pot is embedded in the ashes, in order to avoid the full temperature of the furnace and insure a slow cooling of its contents.

The pots used, of local manufacture, have a life of 300 to 360 hr. The furnace is cheap and easy to build; the operation requires no great amount of skill nor experience, and the Chinese believe that these advantages more than outweigh the inefficiency of the intermittent working. Furnace and pots are illustrated in Fig. 1.

At different places in Germany, Hungary, and France liquation of crude is conducted in a still more primitive fashion. The pots are heated by being placed on the

fuel in an open fire. The upper or charging pots are made of fire clay and are of varying sizes which hold from 10 up to about 40 lb. The lower pots or receivers are made of burnt clay, and are deeply embedded in the ashes of the fire. The pots are arranged in rows, each row (twenty to thirty pots) being separated from the next by a brick wall. The space around the pots is packed with fuel. The receivers are emptied at convenient intervals, and the residues in the charge pots are found to contain usually more than 12 per cent sulphide, which is treated as low-grade ore for white oxide, and then for metal when the antimony market is high. The time required for one shift of the pots varies according to the amount of the charge, generally from 2 to 12 hr. The accompanying sketch (Fig. 2), taken from the book on antimony by C. Y. Wang, illustrates this method as employed at Wolfsberg in the Harz.

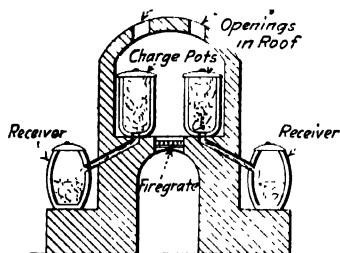


FIG. 3.—Arrangement of liquating pots inside furnace.

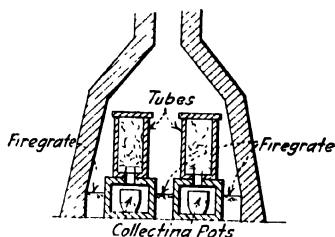


FIG. 4.—Continuous tube-liquating furnace.

By placing the pots in a furnace instead of in an open fire, heat is conserved, fuel is economized, and it is possible to work with lower grade ores. The pots containing the charges are placed alongside of the fire grate and the receivers are placed either directly below the bed of the furnace and surrounded by sand, or better still, they are placed outside of the furnace altogether and connected by clay pipes to the bottom of the charge pots. The advantage of the latter method is that the receivers can be emptied whenever necessary without interrupting the working of the furnace. Figure 3 illustrates the method.

**Continuous Liquation in Furnaces.**—Intermittent working is expensive in fuel and uneconomical in results. Better results are obtained by the continuous working of tube or reverberatory furnaces. The tube furnace is illustrated in Fig. 4.

The furnace is brick, the inside being fire-brick. Three fire grates completely surround the tubes, which are arranged in groups of four. The tubes are over 3 ft. high and are 10 in. diameter at the top tapering to about  $7\frac{3}{4}$  in. at the bottom. The tube walls are approximately  $\frac{3}{4}$  in. thick. In the side of each tube is a small hole through which the residue can be removed. During working hours these holes are closed up with a clay plug. Underneath the tubes are little chambers containing the receiving pots which may be either as shown in sketch or placed on a carriage provided with wheels. The charge for each tube is about 5 cwt., a charge requiring about 3 hr. for complete liquation. The yield is only about 50 per cent of the sulphide content. If coal is used, the fuel consumption is about 65 per cent of the sulphide production; i.e., 65 cwt. of coal are burned in liquating out 100 cwt. of sulphide.

Continuous liquation is sometimes carried out in ordinary reverberatory furnaces with a tap hole placed at the lowest point in the bed for tapping the molten sulphide. The advantages are:

- (1) Less expense for fuel; (2) less labor required; (3) furnaces require less repairs; (4) large quantities of sulphide can be produced in a short time.

The disadvantages are:

(1) Cost of plant is heavy; (2) there are very heavy losses due to volatilization during the operation. The volatilization can be offset by using the Herreshmidt condensing apparatus. Figures 5, 6, 7, and 8 show the construction of a liquation reverberatory.

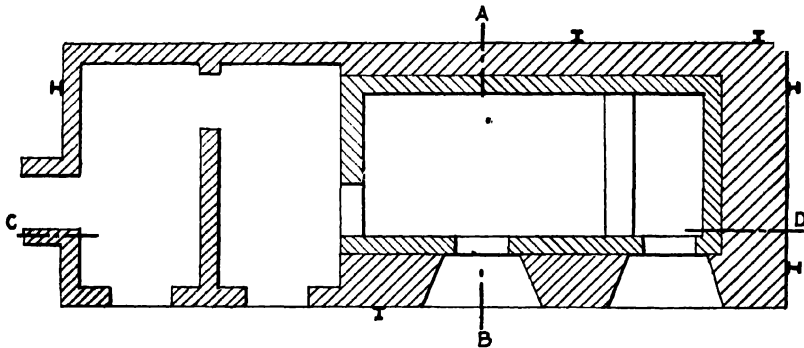
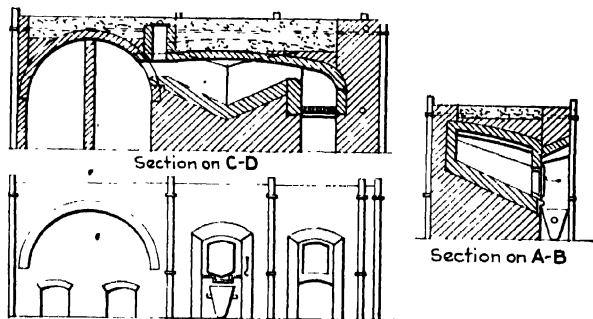


FIG. 5.—Plan of liquating reverberatory furnace.



FIGS. 6, 7, 8.—Elevation and cross sections of liquating reverberatory.

A typical analysis of Hunan crude<sup>1</sup> is as follows:

Analysis		Calculated composition	
Insoluble . . . . .	0.05	Insoluble . . . . .	0.05
Fe . . . . .	0.70	FeS . . . . .	1.10
S . . . . .	22.45	Sb <sub>2</sub> S <sub>3</sub> . . . . .	77.17
O . . . . .	3.18	Sb <sub>2</sub> O <sub>3</sub> . . . . .	19.08
Sb . . . . .	73.56	Sb (met) . . . . .	2.54
	99.94		99.94

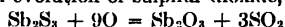
<sup>1</sup> SCHÖELLER, "Blast-furnace Smelting of Stibnite," 1918.

**Preparation of the Stable Tetroxide.**—The method to be followed in the production of antimony metal is selected in accordance with the quality of the ore to be smelted. By far the greater part of the antimony regulus of commerce is produced by methods which involve, first, the preparation of oxides, and, later, their reduction to metal.

Low-grade ores, such as are found in parts of Hunan Province, China, cannot be profitably smelted direct into metal. These ores are converted first into oxides, and then reduced in reverberatory furnaces. Rich ores, however, may be converted into metal by direct methods, but in China, it is a more common practice to convert the richer ores into crude form, oxidize the crude into oxide in reverberatory furnaces, and then reduce it into metallic antimony.

Low-grade ores are more plentiful than rich ores, and the process of oxidizing the ore and then reducing the oxide to metal thus becomes the most important of the methods to be considered.

The oxidizing roasting of antimony ore results in either one of two products, depending on the temperature and air control—the volatile trioxide ( $\text{Sb}_2\text{O}_3$ ), or the stable, non-volatile, tetroxide ( $\text{Sb}_2\text{O}_4$ ). The chemical changes taking place in the production of these two oxides are as follows: On being heated a trifle above  $350^\circ\text{C}$ ., the trioxide is formed, with evolution of sulphur dioxide,



A part of the trioxide is further oxidized to the pentoxide ( $\text{Sb}_2\text{O}_5$ ), which, combining with some of the trioxide, forms the tetroxide ( $\text{Sb}_2\text{O}_4$ ). When oxides of other metals are present, antimonates are formed. If, also, sulphides of foreign metals are associated with the stibnite, these foreign metals are brought mostly to the form of antimonates, instead of remaining, as they would under ordinary circumstances, as sulphates. If the proper temperature (about  $350^\circ\text{C}$ .) and an excess of air have been maintained, and if, in the case of rich ores, constant rabbling has been performed, the roasted mass should contain the tetroxide principally. Under ordinary working conditions, however, the product will contain antimony glass, undecomposed stibnite, and antimonates, arsenates, and sulphates of the foreign metals present. Much attention must be paid to the regular rabbling of the charge as the richer parts of the ore tend to liquefy and to frit together. The richer the ore, the more difficult it is to roast.\* Toward the end of the roasting, the temperature should be raised a little, in order to complete the oxidation of any undecomposed sulphide. If carried at too high a temperature, however, the mass will frit together, and the penetration of air to the interior is prevented, and both the sulphide and oxide are volatilized.

A charge properly roasted has a reddish color while in the furnace, and an ashy-gray color on cooling, and there should be no evidence of fritting in the furnace. If an excess of air has not been available, the roasted product will be largely the volatile trioxide instead of the tetroxide.

The roasting of stibnite for the production of tetroxide is generally carried out in reverberatory furnaces, provided with condensing apparatus. The furnaces are of two kinds: (1) small rabble furnaces (egg-shaped hearth); (2) long-bed reverberatory furnaces (similar to the hand-reverberatories of lead smelting practice). Figure 9 shows the small-type rabble furnace used in China and France.

A rabble furnace of this type handles a charge of 5 to 6 cwt. of ground and screened ore in about 6 hr. The time required varies from 3 to 12 hr., according to richness of ore. During the first 2 hr. the door must be closed, but toward the end it is opened for stirring and rabbling the charge, and for free admission of an excess of air. Loss of antimony in this furnace treatment varies from 4 to 8 per cent.

The long-bedded reverberatory of German, French, Italian, and American plants is about 40 ft. long by 76 in. wide. It has eight or ten working doors on each side,



and carries about  $1\frac{1}{2}$  tons of ore, of which 6 cwt. are charged at a time. The ore works through the furnace in about 40 hr.; during the last 2 hr. before drawing, the charge is thoroughly rabbled every 5 min., and the heat is strong. Properly roasted ore has a dull grayish-yellow color. Loss of antimony in these long-hearth furnaces runs about 8 per cent.

Furnaces with a trough-shaped hearth, sloping toward one side, have been proposed, but are not in successful use, for the carrying on of both reduction and roasting at the same time. The slope of the hearth is for tapping out any accumulation of sulphide that liquates during the roasting.

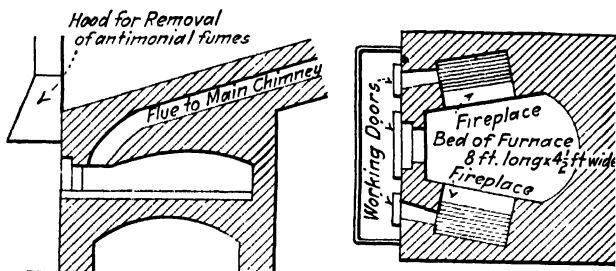


FIG. 9.—Long-bedded reverberatory.

**Preparation of the Volatile Trioxide.**—When it is desired to produce the volatile trioxide of antimony, recourse is had to the process of volatilizing roasting. In this method the admission of air is restricted and higher temperatures are required. The trioxide is readily formed by admitting steam at a high temperature, and at the same time the hydrogen combines with the sulphur in the stibnite to form hydrogen sulphide. The many advantages of this method have brought it into general favor and it is extensively used in one form or other in France and China. These advantages are:

1. Arsenic oxide is more volatile than antimony trioxide and can therefore be separated out.
2. When the ores contain precious metals these are generally found in the residues after volatilization.
3. It is the only method really suited to low grade ores.
4. Condensation is more efficient and loss is almost eliminated.
5. Less fuel is required, as the sulphur in the ore can be utilized as fuel.
6. The condensed trioxide can be reduced to metallic antimony, or it can be marketed as white oxide without further treatment to make paint, enamels, etc.

Of the several modifications that have been developed in the volatilization method of producing of antimony trioxide, the work of Herrenschnidt stands out most prominently. Production by the volatilization method was first accomplished in France, in 1844, by Bobierre, Rousseau and Ruolz, and gradual improvements were developed from that time up to 1881, in which latter year Herrenschnidt patented a practical and efficient method, which he later greatly improved.

**Herrenschnidt Process.**<sup>1</sup>—In the first development of the Herrenschnidt process (1881), a low grade ore, say 20 to 25 per cent antimony, was placed in a blast furnace or cupola with about 10 per cent of coal. For an oxide ore a larger percentage of coal was needed. In this furnace the ore was roasted to produce the volatile trioxide, which passed from the furnace into a condensing chamber

<sup>1</sup> Data on Herrenschnidt process from article by Li, K. C., "Antimony, Its Metallurgy and Uses;" and WANG, DR. C. Y., "The Metallurgy of Antimony."

directly connected to the furnace. Any trioxide not being condensed in the condenser passed on to a reservoir containing water, and was there condensed. The air necessary for oxidation was drawn in by a fan operating at the far end of the water reservoir. Part of the oxygen drawn in combined with the sulphur in sulphide ores to form sulphuric acid.

The chief fault in this process was that the condensation was not so efficient as it might have been, and some years later, in 1903, the inventor took out another patent which was a very decided improvement on his first one. He saw that the condenser must possess a very large cooling surface, have great facilities for deposition of the oxide and also be able to subdivide the current of volatile oxide. All these were provided for in his patent of 1903. Below is a sketch of the complete apparatus (Fig. 10).

In this later Herrenschmidt apparatus (1903), the ore is charged into the furnace (a) where it is melted to produce the oxide. A fan (h) draws the volatile oxide into the flues (b) as shown by arrows, then through a series of condensing tubes (d). Any uncondensed oxide passing through the fan is absorbed by the

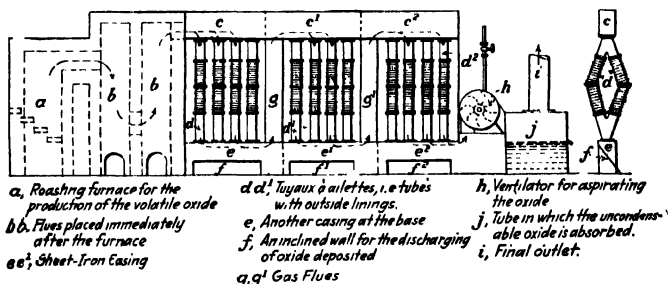


FIG. 10.—Early Herrenschmidt volatilization and condensation apparatus.

water contained in the tank (j). The tubes are covered on the top by the casings (c) while underneath the tubes are other casings (e). It should be noted that the oxide has to traverse a very tortuous path, and in so doing it comes in contact with a very large cooling surface. The lower cases (e) are provided with inclined walls (f) which greatly facilitate the removal of the condensed oxide. The transverse section on the right of the main sketch gives a better idea of the tubing and the manner of removing the condensed oxide.

In 1908 Herrenschmidt again improved on his previous patents. The furnace was improved and the flues between the furnace and the condensing pipes were eliminated, so that the oxide passed direct from the furnace to the condensers. The casings over the tops of the pipes were discarded, and the pipes were joined together at their tops to form a series of inverted V's; in addition to these improvements, two ventilators were introduced, and any volatile trioxide passing through the fans was condensed by coming in contact with water sprayed down at intervals through a coke tower.

Figure 11a is a longitudinal section and view of Herrenschmidt's finally perfected equipment (1908). Figure 11b is a cross-section of a roasting furnace along ab. Figure 11c is a horizontal section along JY.

The broken ore, carrying 10 to 20 per cent of antimony, is charged, mixed with from 4 to 8 per cent charcoal, into the roasting furnace, *a*, the bottom of which is formed by horizontal iron bars *b*. The volatile antimony trioxide is deposited on condensation pipes *e*, in the condensing chambers *d*, under suction from the two fans *h*. The last trace of the uncondensed oxide is caught by the water coming from the coke tower *i*, at the top of which are the water pipe *j*, and the seesaw water distributor *k*. The roasting furnace is built partly of bricks and partly of cast metal. The condensing chambers are of cast iron, and the coke tower of wood. Each condensing chamber is 1 m. long.

With mine-run ores, carrying 10 to 15 per cent of antimony, 6 tons can be treated in 24 hr., with a fuel consumption of 4 to 5 per cent of gas coke, or 6 to 7 per cent of charcoal. With ores containing 18 to 20 per cent of antimony,  $4\frac{1}{2}$  tons per 24 hr. can be treated with fuel burden of 5 to 6 per cent of gas coke or 7 to 8 per cent of charcoal. Each unit employs four workmen per 24 hr., and fans and pump require 3 hp.

Gas coke gives better results, if obtainable, but most of this antimony work is done in out-of-the-way places, where charcoal is cheaper.

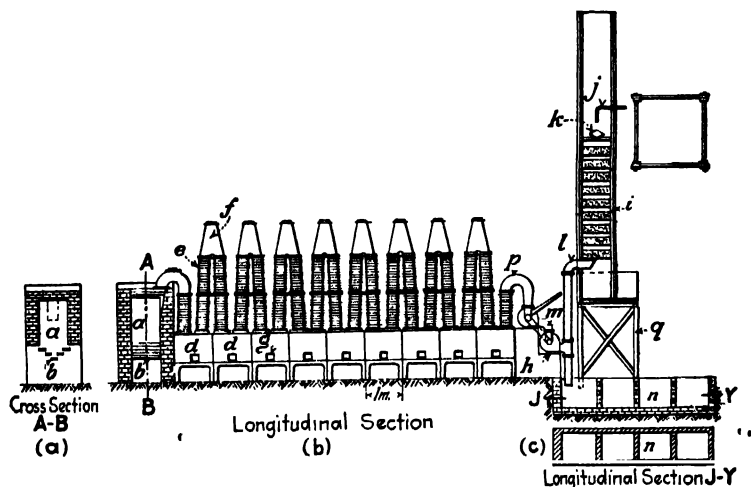


FIG. 11.—Perfected Herreshmidt volatilization and condensation apparatus.

Size of ore treated is from 1 to 4 cm. Ore dust must be separated out, and, if present in large quantity, must be briquetted with 7 or 8 per cent clay into balls of proper size, and charged along with the ore. The working of the furnace proceeds as follows:

A charge of old scoria is placed on the grates up to a height of about 10 cm. above the uppermost bar; and wood and charcoal are put in to a height of another 10 cm. As soon as the fuel is lighted and burning freely, another charge of 300 kg. of scoria, mixed with 6 per cent of charcoal, is put in. Finally, when the furnace is up almost to full heat, an ore charge of 50 kg., mixed with 2 kg. of charcoal, is put in, and this is continued until the furnace is full to within 30 cm. from the mouth. The same charge is repeated every 12 to 14 min., according to the rate of revolution of the ventilating fans—which is from 1,200 to 1,400 r.p.m.—and the scoria is discharged accordingly.

The temperature of roasting, for trioxide production, should not be over  $400^{\circ}\text{C}$ . About 30 cu. m. of water per day are required for one apparatus.

The loss of antimony in the Herreshmidt apparatus is variable, approximating 10 per cent; the skill of the laborer is all important. By manipulation and spreading

of ore and fuel so that the ore is thoroughly burned and the antimony contents fully volatilized, the percentage of fuel can at times be cut down to about 3 per cent, and the yield of oxide can be increased to 95 per cent.

The Wah Chang Mining & Smelting Co.'s plants in China, for several years the leading producers of antimony, used about 15 per cent charcoal on ore running 20 to 35 per cent of antimony; if the charge consisted of liquation residue the charcoal required amounted to 20 to 22 per cent for coarse, and 24 per cent for fine. The scoria discharged from the shaft furnaces generally carried about 3.5 per cent of antimony, from ore charges; and 4.5 per cent of antimony, from the liquation residue charge.

The ideal ore for volatilization treatment in shaft furnaces is one with an antimony content of 15 to 25 per cent. When the ore runs over 40 per cent in antimony, the latter partly volatilizes and partly liquates, and part of the liquated product combines with the volatilized trioxide to form antimony glass (an oxysulphide compound) which causes fritting at the lower zone of the furnace. Even with ore carrying 30 to 35 per cent of antimony, this fritting occurs to some extent, necessitating the maintenance of a higher temperature in the furnace than is necessary for poorer ores. The richer the ore the higher the percentage of fuel required for the charge.

It is possible to volatilize ores carrying up to 20 per cent of antimony with 6 per cent of charcoal, the temperature being kept at a low red heat. On the other hand, if the charge be liquation residues, ranging from 15 to 25 per cent antimony content, a different problem is presented. This material makes a charge that partially blocks up the furnace at a very low, red heat, and prevents the free passage of air. To remedy this, some works use a forced draft, and others resort to an excess of coke to increase the porosity of the furnace burden—as much as 30 to 50 per cent of the charge. It is possible to tell when the furnace is blocked, or when the suction fan is choked with trioxide, by observing the appearance of a reddish tint in the trioxide fume, which issues white if furnace conditions are normal. This reddish fume is a hydrated sulphide, resulting from sulphide particles which have been volatilized at temperatures above 550°C. in the absence of sufficient free oxygen. On taking up moisture from the ore, these sulphides take the hydrated red form (probably  $\text{Sb}_2\text{S}_3 \cdot 2\text{H}_2\text{O}$ ).

**Other Processes for Preparation of the Trioxide.**—There are perhaps a dozen processes for the preparation of the volatile trioxide, which at different periods, in France, Italy, and Germany, have had some prestige.\* In all of them, the principle of roasting, volatilizing, and condensation of the oxide is, of course, the same; differences exist merely in the forms of furnaces, condensers, and methods of collecting the oxide.

In the Chatillon and Società Anónima processes, which have been in successful operation in France and Italy, the oxide is filtered through cotton or linen bags. In most of the other processes, the oxide produced is, in manner similar to that described above under the Herrenschildt method, condensed either in long flues, on baffles, in condensation chambers, or by use of water.

In the Chatillon process, which has been employed on a large scale in France, the furnace consists of two double cupolas terminating in a common flue from which the volatilized oxides are led to water-cooled condensing chambers made of sheet iron. The upper cupolas are charged with alternate layers of fuel and ore, and as the liquated sulphide melts and falls through to the lower cupola, it meets an upward current of hot air which converts it into the trioxide ( $\text{Sb}_2\text{O}_3$ ). Before leaving the plant the gases are reduced to a temperature of 100°C. and passed through a baghouse. The sublimate obtained contains 98 to 99 per cent antimony trioxide.

The Plews process (1902), one of the best known of the volatilizing methods outside the Herrenschildt process, proceeds as follows: Stibnite, crushed to less than

1-c.c. size, is charged into an ordinary type of rotary furnace, which has been previously heated to a dark red, by means of any smokeless fuel. An oxidizing flame is then produced in the furnace, and the temperature is raised to a light red, and so maintained until all the volatile oxide is given off. With certain minerals, the antimony is not easily volatilized by an oxidizing flame; in this case, alternate periods of oxidizing and reducing flame are maintained as long as necessary. The oxide is drawn off into condensing chambers by means of a fan, in the usual way, and the last traces of uncondensed oxide are absorbed by contact with water. The fuel used is coal gas or oil gas generated in a gas producer. Figure 12 shows the arrangement of the Plews apparatus.

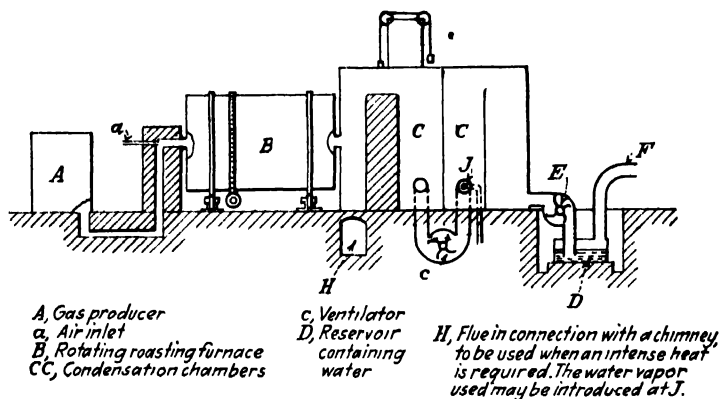


FIG. 12. Plews volatilization process.

**Methods for the Production of Metallic Antimony.**—The last phase in the metallurgy of antimony is the production and refining of metallic antimony. Unrefined antimony metal is sometimes called crude antimony, but the metal is never marketed in this form; the name would be confused with liquated sulphide which is commonly called crude antimony, or more correctly *antimony crudum*. Antimony metal may be obtained from: (1) the oxides (trioxide or tetroxide); (2) from *antimony crudum*; or (3) by direct smelting of antimony ores. Of these methods, the bulk of the world's antimony, up to the present time, has been produced by the first two mentioned.

The direct smelting of metal from its ores was receiving a great deal of attention, however, in the United States (San Pedro); Mexico, (Wadley); and England, during the period just preceding 1918, and in earlier years at Banya in Bohemia, and some very successful results were being achieved. It is not overstating the case to say that the operators of the blast furnaces engaged in this direct smelting had, prior to the great metal depression, already accomplished such progress in the normal blast-furnace reduction of antimony ores as to indicate the possibility of a complete reconstruction of the practice of antimony metallurgy. It is well demonstrated that the blast furnace is the best appliance for a certain class of antimony ores—those containing about 25 to 40 per cent of metal. These are too high to be best suited for roasting, and are yet too poor for liquation or direct precipitation smelting, and for their treatment, as well as for by-products of the same richness, the blast furnace offers undoubtedly the best method.

Under the methods which have, in general, so far prevailed, reduction of the oxides is carried out either in reverberatory furnaces, in water-jacketed or blast furnaces,

or in crucibles. In reducing the oxide, care must be taken to control volatilization and to keep any unaltered sulphide out of the mass of metal. A fusible slag is utilized, which forms a cover preventing volatilization, and which also dissolves any metallic sulphides left. This slag, composed of soda, potash, and Glauber's salt, acts as a refining agent, carrying off most of the impurities which may be in the oxides. On ores carrying low percentages of antimony, the volatilization and reduction processes are used, because they are considered to be the cheapest of all methods and produce a very pure metal.

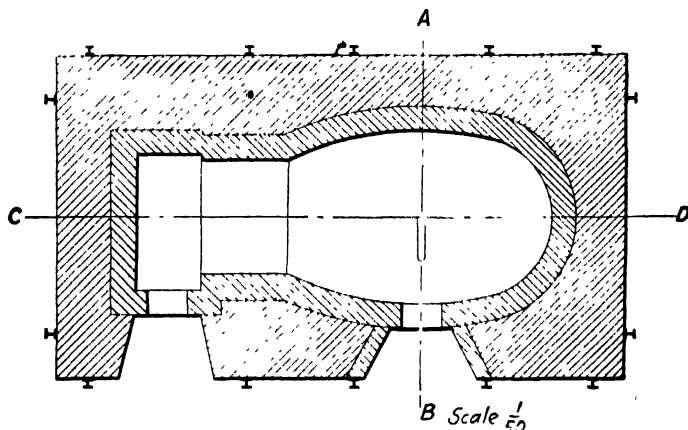


FIG. 13.—Plan of reverberatory for reduction method.

**Reduction of Oxides in Reverberatory Furnaces.**—Of the several reduction methods, the reverberatory is simple and easy to control, but is attended by heavy loss of antimony, and is therefore used for rich ores and cheap fuel. Loss of metal generally runs from 12 to 20 per cent and may be as high as 30 to 40 per cent with careless working. In France, Austria, and New Jersey, the reverberatories used have been of approximately the following dimensions: hearth

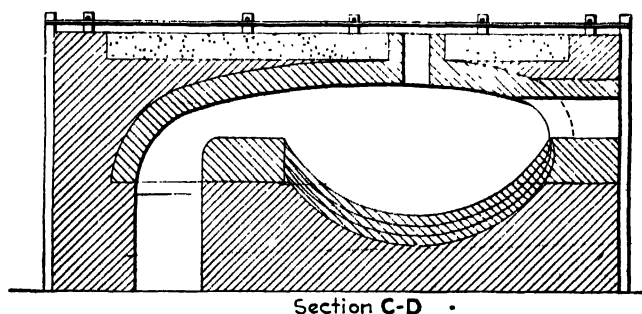


FIG. 14.—Section of reduction reverberatory.

egg shaped, length about 8 ft.; width in center 5 ft. 3 in.; width at fire bridge 3 ft. 4 in.; height of fire bridge 1 ft. 4 in.; width between top of fire bridge and roof 1 ft. At the deepest part of the bed is a hole through which the metal is tapped. An 8-in. flue leads into condensing chambers about 400 ft. long. The antimonial vapor passes into these chambers and is there deposited.

Figures 13, 14, and 15 show the type of furnace used.

The precipitate recovered in the condensing chambers contains up to 50 per cent of antimony. The furnace charge consists of about 500 lb. of roasted ore, oxidized ores, oxides, liquation residues, flue dust, etc., together with about 100 lb. of flux composed of salt, soda, about 70 lb. of ground charcoal, and sometimes a small quantity of Glauber's salt. It is also found to be good practice to remelt about 300 lb. of slag from previous charges. The flux is charged into the furnace first, and when it is melted down and all boiling or agitation of its surface has ceased, the other materials are charged into the furnace, about 40 lb. every 15 or 20 min. The charge is then well

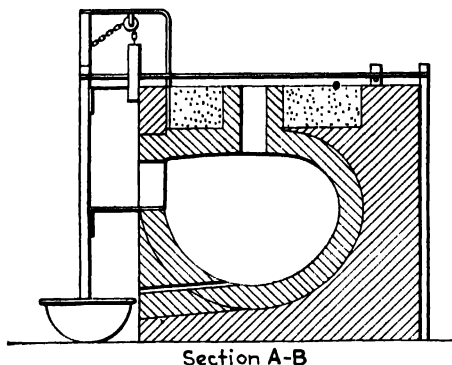


FIG. 15.—Section of reduction reverberatory.

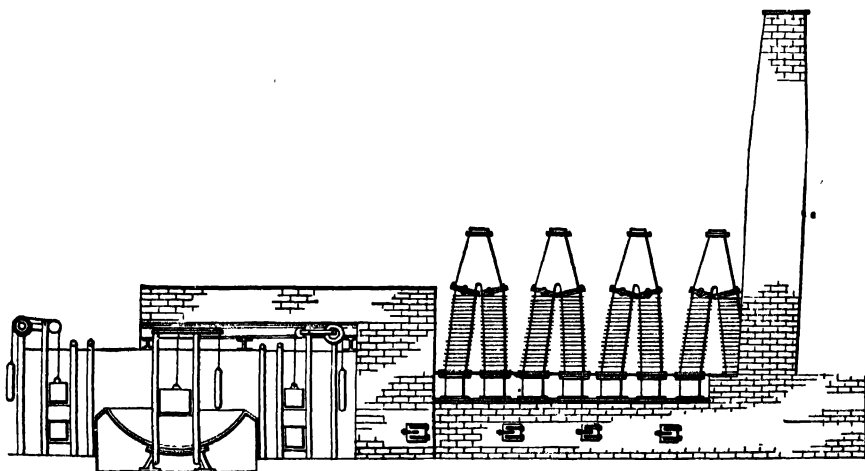


FIG. 16.—Reverberatory furnace provided with Herrenschildt condensation apparatus.

stirred, and the scum produced is drawn off. After the last charge has been put in, the temperature of the furnace is raised and kept up until the process is completed. During the smelting, the charcoal acts as a reducing agent, robbing the antimony of its oxygen, while part of the soda combines with the sulphur, and the remainder helps to form a slag with the gangue. Any other metals present are carried into the slag as sulphides, by the action of the sulphide of soda which is produced through the reduction of the Glauber's salt by the charcoal. Common salt serves the same purpose by carrying foreign metals into the slag as chlorides.

The fuel consumption is somewhere between 5 and 6 cwt. per charge and the loss is usually about 14 to 15 per cent. When considerable antimony sulphide is present, a little iron or iron slag may be added to assist in reducing the sulphide. When the smelting is complete, the metal is drawn off into molds through a tapping hole, and during the cooling in the mold, care must be taken to have it completely covered over with slag. When the metal solidifies, the slag is knocked off by hammering.

The trioxide produced by the volatilization method can be reduced in an ordinary reverberatory furnace provided with the Herrenschmidt condensing apparatus shown in Fig. 16. The furnace is first heated, then charged with the following: 10 parts of trioxide; 6 parts of sulphide (crude); 1 part of carbon (charcoal or anthracite).

The charge is thoroughly rabbled after about 6 hr. in the furnace and the metal separates out from the slag and is soon ready for tapping into molds. The "starring" of the regulus is done in the mold. A purifying mixture, composed of 6 parts of carbonate of soda and 4 parts of antimony trioxide, is melted down in a small chamber at one end of the reverberatory furnace. When the metal is ready to be tapped some of this molten mixture is poured into the molds to be used. The regulus is then run into these molds, and the purifying mixture, being lighter, immediately comes on top forming a cover over the regulus. When the metal solidifies, any of the mixture remaining on top is removed by hammering.

**Reduction of Oxides in Water-jacketed Blast Furnaces.**—In California and Mexico, blast-furnace smelting of antimony ores has been brought to a high degree of efficiency. The manipulation of the furnace and charge has much in common with the ordinary practice of the lead blast furnace.

Roasted ore, briquetted flue dust and oxides, and smaller amounts of unroasted stibnite, together with siliceous waste for slag-forming material, make up the charge. Recovery of antimony runs 95 to 98 per cent, slags carrying about 1 per cent, sometimes running as low as 0.25 per cent of antimony.

The Cookson plant, at Wadley, Mexico, handles ores of a refractory nature and of comparatively low grade. The antimony content varies from 25 to 40 per cent. The ores at Wadley are, in the main, oxidized, between 80 and 90 per cent of the antimony being present as oxide, the remainder being sulphide. The gangue is siliceous and calcareous. On account of the refractory nature of the ores and their oxidized condition, the comparatively simple methods of smelting adopted in China are not satisfactory, nor can the usual English methods be employed. They have, however, proved amenable to blast-furnace treatment. The plant is somewhat elaborate and costly, in comparison with the reverberatory methods, but excellent smelting results are obtained. The plant is seldom in operation with antimony below 12 cts. per lb., c.i.f. New York.

The ores, after rough concentration, are smelted in rectangular water-jacketed blast furnaces, very similar to those employed in smelting lead ores. Limestone and iron ore are used as fluxes, and coke as the reducing agent. The blast furnaces are some 28 ft. high, 5 by 3 ft. hearth area, and are blown by compressors delivering air at a pressure of from 2 to 3 in. of mercury. A forehearth is provided to separate the metal from the slag. Owing to the high temperature attained in the blast furnaces, and to the volatility of antimony, very efficient bag houses are necessary to deal with the fume carried over in the blast-furnace gases. The fume is briquetted and worked off with the ore in the blast furnaces. By running a highly siliceous slag the antimony content of the slag is kept down to about 1 per cent.

The antimony obtained as above, generally termed "singles," contains from 5 to 7 per cent iron and 1 to 2 per cent sulphur. Deleterious impurities are practically absent as the ores, apart from their low grade, are very pure.



The iron and sulphur in the singles are removed by submitting the metal to the "doubling" process, which consists of a combination of liquation and fusion under alkaline fluxes in reverberatory furnaces. The resulting "doubles" are further refined and starred by Cookson & Co.'s special starring process, the resulting "Star" antimony being of high quality and guaranteed 99.6 per cent purity.

**Reduction of Oxides in Crucibles.**—This method of reduction is adopted only for very rich ores or when crude antimony or the trioxide is used to produce the metal. The use of crucibles and pot furnaces precludes the working of large charges. The roasted ore is fused with 10 per cent of its weight of crude argol, or with charcoal or anthracite and potash or soda, in fire-clay crucibles, heated in a wind furnace. The mold in which the melted metal is cast must be coated with tallow or with fire-clay cream.

A typical charge for one crucible is as follows: roasted ore, 26.5 lb.; charcoal (10 per cent), 2.6 lb.; soda (7.15 per cent), 1.9 lb. Ten or twelve pots are placed in a single furnace, each pot turning out four or five charges in 24 hr. Fuel consumption is 70 to 80 per cent of the weight of ore. Each pot has a life of seven or eight charges.

A type of furnace used in the Herreschmidt operations, for reduction to starred regulus, from balls, or briquettes, composed of antimony oxide, powdered anthracite, carbonate of soda, and water, is shown in Fig. 17.

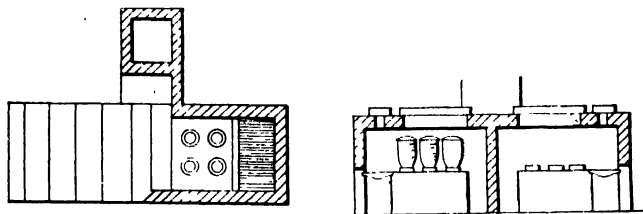
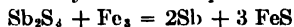


FIG. 17.—Furnace for reduction of oxides in crucibles.

**Extraction of Metal from Crude.**—Antimony crude or antimony "needle" is frequently marketed and used for various purposes, such as for vulcanizing rubber, match making, and for ammunition manufacture. As the market for crude is limited, it is necessary to convert the greater part of it into antimony regulus. This may be done in one of two different ways: (1) conversion of the sulphide into antimony oxides, and then reducing the oxides in reverberatory furnaces, (2) direct smelting of the sulphide to metal, iron being added as the reducing agent.

**English Precipitation Method.**—In China, the English precipitation method has been found too inconvenient and costly to compete successfully with the oxidizing methods, and the latter have become the accepted mode of treatment for crude in that field. In England, Hungary, Japan, and Mexico, however, the precipitation method is in vogue, rich ore or *antimony crudum* being directly reduced to metal by crucible fusion with metallic iron. The fundamental principle involved in this method is the greater affinity of *sulphur* for iron than for antimony.

In the precipitation process iron is used to decompose the sulphide of antimony to give sulphide of iron and antimony as in the equation:



Iron sulphide is formed, even at a comparatively low temperature, the antimony being separated out in the metallic state. The high specific gravity of the

iron sulphide makes it difficult to separate the antimony from the iron sulphide, and it is necessary to add sodium sulphate and carbon in order to produce sodium sulphide, which, combining with the iron sulphide, forms a fusible matte of low specific gravity. In England, instead of sodium sulphate and carbon, common salt is used. The iron is usually added in the form of turnings, shavings, or tin-plate cuttings. The proportion of iron must be carefully controlled, for if sulphides of lead and arsenic are present, they will be reduced by any excess of iron not taken up by the stibnite, and enter into the antimony metal as impurities.

It is found in practice that the theoretical amount of iron required for desulphurizing the stibnite is not sufficient, due to the fact that part of the iron is taken up in decomposing the sodium sulphate.

Losses of antimony in the precipitation method occur from both volatilization and slagging, running 10 per cent, or over. Ordinarily, the process is carried out in crucible furnaces. Shaft and reverberatory furnaces are used in some cases, but the metal losses are much greater in the latter furnaces.

The English process proceeds as follows: The stibnite is reduced by metallic iron in crucibles in a long reverberatory furnace. Dimensions of the furnace are: length, 54 ft.; width (inside), 7 ft. 4 in. The bed is covered by a low arch which springs almost from the surface of the ground, the bed itself being below ground level. It is heated by a fireplace at each end, a common flue taking off from the middle of the furnace floor. Sides and roof of the furnace are covered with cast-iron plates.

The crucibles are lowered into place through 14 in. circular holes in the arch, forty-two holes (twenty-one on each side) being provided. The pair of crucibles nearest the fireplaces at each end is kept for "starring," or refining, the crude metal. Each crucible takes a charge of: ore (hazel nut size), 42 lb.; iron, 16 lb.; common salt, 4 lb.; skimmings (from the doubling operation), or slag from previous smelting, 1 lb.

Tinned scrap is preferred; for insertion into the crucible it is pounded into a round ball, large enough to fit the top of the crucible. The balance of the iron required is in the form of turnings or borings, which are mixed with the ore, together with the salt. The mixture is dropped into the crucible through a funnel; the furnace hole is then closed for half an hour, when the crucible is examined. The salt used assists the separation of the slag, and tends to promote the fusion of the siliceous material. On an average, four meltings are made in each crucible per 12 hr.; the richer the ore, the shorter is the time required.

The crucibles are made of a mixture of graphite and fire clay, and are generally 20 in. high and 11 in. across the mouth. The crucible, dry, weighs 42 lb., of which approximately 36 lb. are fire clay, and 6 lb. graphite.

A mold, conical in shape, is placed opposite each crucible. The metal obtained is known as "singles," and contains about 91.6 per cent antimony, 7.3 per cent iron, 0.8 per cent sulphur, and 0.3 per cent insoluble matter.

The "singles" are next purified by fusion with a small amount of liquated sulphide of antimony, to remove the iron remaining in the metal. The charge for this second, or "doubling," process, is: singles (broken small), 84 lb.; antimony crude, 7 lb.; salt, 4 lb.

The fused mass is stirred occasionally with an iron rod, the time required for one charge being about 1½ hr. When fusion is complete, the slag and matte are ladled off with an iron spoon and the contents of the crucible holed into the molds used in the previous fusion; the matte and skimmings are added to subsequent ore smeltings. The metal thus obtained is known as "star bowls," and contains 99.0 to 99.53 per cent antimony, 0.18 per cent iron, and 0.16 per cent sulphur.<sup>1</sup>

<sup>1</sup> In Japan at the Saijo Smelter, the Star Bowl metal carried 97 to 98 per cent Sb, 1.5 per cent Fe, and 0.7 to 0.8 per cent S.

The effectiveness of this second liquation can be understood when it is remembered that in such an alloy of antimony and iron intermetallic compounds are present. One of these, with the chemical formula  $\text{Fe}_3\text{Sb}_2$ , has a freezing point of  $1016^\circ\text{C}$ ., and another ( $\text{FeSb}_2$ ), which forms from  $\text{Fe}_2\text{Sb}_2$  and liquid, crystallizes out at  $730^\circ\text{C}$ . The melting point of pure antimony is  $630^\circ\text{C}$ . Hence, in the heating up of this alloy, the antimony first melts and the antimony-iron compounds tend to separate and rise to the surface. These are then "taken up" by the slag and removed from the bath of metal under purification.

The presence of sulphur, due to the excess of crude used, is indicated by the crystalline pattern which forms on the surface of the metal being covered with small glistening patches, the latter being known as "flouring."

In order to remove this sulphur, another fusion is necessary. The custom of the trade is to demand antimony that is "starred," or crystallized, on the upper surface, and it is at this stage that this "star" is obtained. These two results are accomplished by melting the metal with what is known as the "antimony flux," a substance which is often difficult to obtain, in proper composition, at first. This flux is prepared by rule-of-thumb method, about as follows: 3 parts of ordinary potash are melted in a crucible, and 2 parts of ground liquated sulphide are mixed in. When fusion has become quiet, the mixture is poured out and tried on a small scale to find out whether it yields a good "star." If the "star" is satisfactory, the ingot of metal obtained is then broken and the metal examined in order to determine whether it is free from sulphur. If, however, a good star is not obtained, the flux is remelted, and more of one ingredient or the other is added as experience dictates.

The first of these operations of the precipitation process—smelting the crude with iron—is called "singling;" the second operation—resmelting the singles for the production of the bowl metal—is called "doubling;" and the last operation is called "refining," or "frenching."

#### **Direct Extraction of Metal from Ore. (*Reverberatory Bath Furnaces*).—**

Several patents have been taken out (Sanderson, Cookson, Herrenschmidt) on the direct smelting of antimony sulphide in a bath of ferrous sulphide, on the hearth of a reverberatory furnace. This method has given good results, but has had no wide adoption commercially. After the hot ore has been charged into the reverberatory and thoroughly rabbled, iron is added, the temperature raised, and, when decomposition of stibnite by iron is complete, the antimony metal is tapped. The tap hole is closed as soon as the iron sulphide appears. Slag is drawn through the working doors, and as the iron sulphide increases during the operation it is removed until the bath is reduced to its original depth.

**Water-jacket Blast-furnace Smelting.**—The blast-furnace smelting of antimony ores, both sulphide and oxide, is entirely feasible, and will undoubtedly come into more common use as the industry advances. Already, in Mexico, California, and England, successful blast-furnace smelting has been under way for several years, proceeding along lines only slightly modified from regular lead smelting practice.

The operators of these blast-furnace plants are most enthusiastic regarding the advantages and ultimate general adoption of this method, asserting confidently that the first page of antimony metallurgy has hardly been written and that the blast-furnace process will extensively replace the old existing methods in the industry. That this may come about in Europe, Mexico, and America there is little question. Under existing ownerships and conditions in China, however, it is extremely improbable that any reshaping of the industry will take place.

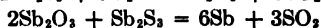
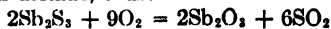
Attempts to smelt unroasted stibnite ores in water-jacketed blast furnaces did not come to any successful result until in recent years, and published information on the subject is exceedingly meager. There is a marked difference in the behavior of stibnite and that of other metallic sulphides in the blast furnace. It has been found best to add no metallic iron to the charge, and to regulate the coke so as to preclude any reduction of ferrous oxide in the flux. No iron available for matte is provided, and matte is usually absent. Any addition, or presence, of metallic iron will always result in the production of an antimony-iron alloy—speiss.

It is usually found that the contents of the furnace crucible gradually freeze from the bottom upwards, and the entire crucible is eventually a solid mass. It is frequently a practice to fill the crucible with fire brick, and separate the mixed flow of slag and metal in a shallow reverberatory forehearth.

While the blast furnace smelting of stibnite is as yet in an experimental state, it is to be stated that the best conditions for the process appear to be: less than 10 per cent of coke, low blast pressure, low metal content of the charge (about 10 per cent), high smelting column (over 15 ft.), and separation of slag and metal in a heated forehearth. In an efficient plant, the great bulk of the volatilized material is recovered in bag houses, but it is, of course, undesirable to have to retreat a large amount of fine material unsuitable for blast-furnace work. The flue dust is best treated in a reverberatory, while the fume is useful in refining, or it may be used as raw material for the manufacture of antimony compounds.

The blast-furnace process does not appear to be adapted for the treatment of high-grade stibnite ore. Loss by volatilization is common to all forms of antimony smelting, and in this respect the blast furnace is far worse than the reverberatory, where a layer of flux or slag protects the metal. With low-grade material, however, which it is difficult or wasteful to treat by other methods, the blast furnace offers decided advantages, *i.e.*, where large quantities of poor ores, foul slags, mattes, or liquation residues have to be worked up. It is a favored mode of smelting for all materials containing about 25 to 40 per cent of antimony, which can be mixed with fluxes to give a charge sufficiently poor in metal to hold down volatilization.

It is believed by Schoeller<sup>1</sup> that the production of antimony from stibnite in the blast furnace is an oxidizing process in which the metal is formed in two stages which proceed simultaneously: first, the molten stibnite absorbs oxygen from the blast; secondly, the oxide at once reacts with the unaltered sulphide (Roast-Reaction process) to form metal and sulphur dioxide, thus:



In endorsing this theory of the blast-furnace process it is realized that it has been a commonly held belief that antimony sulphide and trioxide do not react on each other as do the corresponding lead and copper compounds, but that the antimony compounds fuse together to an antimony glass. The latter reaction occurs, without question, if the oxide-sulphide mixture be fused in a crucible under a layer of salt, but if stibnite is roasted with insufficient access of air, some oxide will be formed which will react with the unaltered sulphide, part of the antimony settling out in a metallic state. The roast-reaction process does, therefore, have a part in the smelting of antimony. It appears, in some degree as well, in the process of liquation, the metallurgical operation carried on on a large scale in China, for the concentration by fire of antimony sulphide ores. Examination of this crude discloses the fact that it is not pure antimony sulphide, but a complex solid solution, containing oxide and free metal. The molten sulphide in trickling down from the upper pot absorbs oxygen from the air rising from the crude already collected, which partly converts it to trioxide. This reacts with more sulphide to form metal and  $\text{SO}_2$ , which latter is carried away by the

<sup>1</sup> "Blast-furnace Smelting of Stibnite," *Trans. I. M. M.*, (1918).

draft, allowing the reaction to proceed. Once the material has collected in the lower pot the reaction is arrested on account of the lower temperature and the small surface exposed. It is thus proved that molten antimony sulphide by itself, in an air current, is partly converted into antimony, and the product also contains the trioxide.

**Converters.**—Sulphide ore of antimony can be smelted in a converter into which air is blown, but this is not a method in practical use. The air burns part of the sulphur of the ore, with the production of sulphurous acid and the metal itself. Antimony sulphide fumes are formed also, and these, if acted upon by a current of air, give antimony oxide.

**By-products of Antimony Smelting.**—The by-products produced in the foregoing processes include liquation residues, matte slags, and flue dust. The slags obtained from the extraction by the roasting and reduction method consist principally of silicates; those from the precipitation method, silicates and sulphides. They are thrown away if not sufficiently rich to be used in the first smelting of the ores. The other by-products are all added to the charges in smelting the ores, the liquation dross being first roasted. The flue dust is intimately mixed with lime, before smelting. Liquation residues are also sometimes treated separately in shaft furnaces.

### EXTRACTION BY WET METHODS

The extraction by wet methods of antimony from its ores has had much attention in European centers, but it is still a matter of academic discussion, rather than practical application. Solution of stibnite is readily effected in sodium sulphide, sodium hydroxide, or calcium sulphide, and from such solutions antimony sulphide is precipitated by carbon dioxide or sulphurous acid. There is little evidence, however, that commercial recovery of antimony from its ores by wet methods will come about.

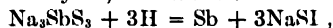
**Electrolytic Extraction of Antimony.**—The supply of antimony for the world's needs to date has come almost entirely through the application of dry methods. Poor antimony ores either have not been used in the past, or have been subjected to a volatilizing roast, with subsequent reduction of the trioxide, usually in reverberatory furnaces.

This is, however, a somewhat laborious metallurgical operation, and the application of electrolytic methods as a means of extraction from poor ores has long been desired.

During the high prices of the years, a small production was made electrolytically, the solvent being a 6 per cent sodium hydroxide solution, which gives an extraction without serious contamination with other metals.

This solution, electrolyzed, deposits antimony of a very high purity, but in ordinary times the deposition of the antimony and the necessary regeneration of the electrolyte are too costly to make the process commercial. The chief difficulty is a troublesome accumulation of thiosulphate at the anode which blocks the commercial success of the electrolytic process.

When the solution is electrolyzed, the reaction at the cathode seems to be:



while at the anode, sodium thiosulphate and  $\text{Na}_2\text{S}_2$  are formed by oxidation. The 6 per cent NaOH solution holds about 3 per cent of antimony at first, but as thiosulphate accumulates, the solvent power decreases until there has accumulated one

atom of sulphur for each atom of sodium present, when the solvent power has dropped to about 0.7 per cent. When this amount of sulphur has gone into solution the iron anode commences to be attacked and falls to pieces rapidly. A practical insoluble anode has not been found. The continuance of the process beyond this point at which the sulphur in solution commences to be in larger atomic percentage than the sodium, requires the regeneration of the solution, or furnishing a new one. If a new solution is applied, it means the consumption of one pound of NaOH per pound of antimony.

The best way to handle this situation seems to be the proposal by Demorest to evaporate the solution to dryness with exhaust steam; roast the residue in a reverberatory furnace to get rid of about half the sulphur, thus changing the thiosulphate to sulphate; then mix with coal and heat until it has all been reduced to  $\text{Na}_2\text{S}$ , which quickly dissolves stibnite and can be put into the circuit again. Small-scale experiment<sup>1</sup> shows this to be successful, but it has not been tried on a large scale.

To summarize, stibnite dissolves easily in NaOH or  $\text{Na}_2\text{S}$ , from which antimony in a high state of purity is precipitated with a current efficiency of about 76 per cent, a voltage of 2.7 giving a power cost about equal to that of the electrolytic production of zinc. The solution must be regenerated or renewed when one pound of antimony has been produced per pound of NaOH used. The electrolyte may be reduced to  $\text{Na}_2\text{S}$  but the practicability of this has not been tried.

Nevertheless, there remain possibilities of using the electrolytic process as an auxiliary method for complex gold-silver-antimony, or copper-antimony ores.

The electrolysis of antimony for refining the crude metal has been studied by A. G. Betts, who came to the conclusion that a fluoride electrolyte offered the best chance of success. Arsenic and gold are deposited with the antimony, however, and, so far as the author knows, the process has not been reduced to a working basis, largely because of this fact.

A current density of 11 amp. per square foot of anode surface gives a clean-cut crystalline deposit, easily scraped from the anodes on which the deposition takes place. Higher current densities cause the deposit to be too compact for facility in cleaning up, while a lower current density causes the deposit to be too flocculent and to fall back into the unprecipitated pregnant solution.

**Refining of Antimony Metal.**—Unrefined antimony metal usually contains sulphur, iron, arsenic, copper, and lead. The latter occurs frequently as it is quite common to find antimony and lead together in ore. Arsenic can be separated out during oxidizing, while the other impurities must be carried off in the slag. Copper and iron can be removed by the addition of antimony sulphide, together with soda or potash, or Glauber's salt and charcoal. The addition of soda or potash also helps to remove sulphur by fusion, and converts arsenic into arseniate of soda or potash. It is somewhat difficult to remove the cad, and when antimony ores are found to contain a considerable percentage of lead, they may, with advantage, be smelted together with lead ores to produce hard, or antimonial lead (12 to 15 per cent Sb).

It has long been the practice of the trade to judge the purity of refined antimony by the development of a fern-like structure, or "stars," on the surface of the ingot. The appearance of this structure does not actually indicate the relative purity of the metal, but is only the result of cooling it slowly under cover of a layer of a properly prepared starring mixture—couverture—a slag which has a fusion point lower than that of antimony, which is 630°C. When the regulus contains impurities like sulphur, arsenic, lead, or iron, to any appreciable extent, its surface shows the presence of these

<sup>1</sup> DEMOREST, D. T., Professor of Metallurgy, Ohio State University.

foreign elements by specks, by a leaden appearance, or by a poorly defined appearance of the fern-like structure. It is true, on the other hand, that regulus containing impurities above what are considered to be the limits imposed by the market, often shows stars as bright and well-defined as those of well-refined regulus. Since buyers demand this artificial adornment on the regulus, the starring operation has become a regular part of the refining process, adding an unnecessary cost of from \$5 to \$30 per ton.

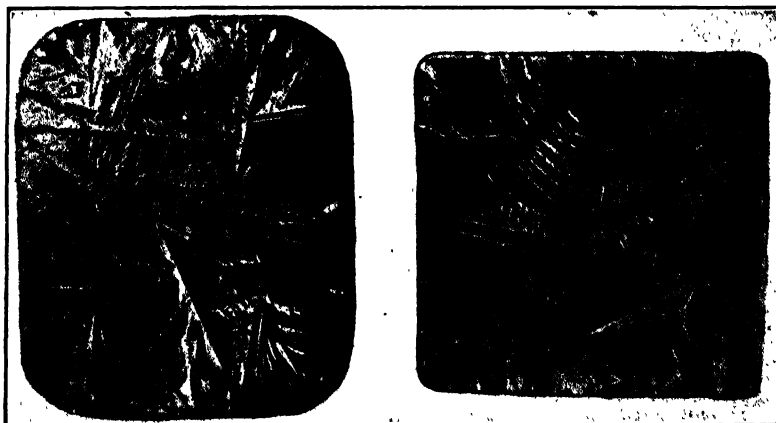


FIG. 18.—Starring on surface of antimony, 99.6 per cent pure.

Different mixtures for this couverture are shown in the following table, by Dr. C. Y. Wang, as used, according to local conditions, by various antimony smelters in China:

COUVERTURE MIXTURES

Ingredients		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
Crude (high-grade)...	$Sb_2S_3$	15	15	2 2	$4\frac{1}{2}$	7	3 to 4	5						6	7
Antimony tetroxide (well-roasted crude)	$Sb_2O_4$	24	24	13 2				30							14
Antimony trioxide...	$Sb_2O_3$				20	18	32		85	4 to 5	8	40	7	$16\frac{1}{2}$	
Potash.....	$K_2CO_3$	10	11	7 5						1 to $2\frac{1}{2}$	1	1			
Soda ash.....	$Na_2CO_3$	1	3		5	4	2 to 4	5 to 6	15			4	1	1	$\frac{1}{2}$
Charcoal.....	C	$1\frac{1}{4}$	$1\frac{1}{2}$	5 7	$\frac{1}{2}$	$\frac{1}{2}$	1	1						$\frac{1}{2}$	$\frac{1}{2}$
Smelters using the mixtures. ....		Pao Tai	Pao Tai	To-cheng	Loong Kee	Tai Wo		Pao Tai	Wah Chang	Wah Chang			Loong Kee	Pao Tai	Pao Tai

<sup>1</sup> Pure flue dust.

Another starring mixture for pure Chinese ores, patented by Wang in 1918, with the object of avoiding the use of mixtures containing any antimony compound, utilizes iron sulphide, which is generally discarded from the precipitation process of antimony smelting as useless. This by-product takes the place of an antimony compound, and is used with any suitable alkali compound, preferably potassium carbonate. The proportions of the mixture are as follows: iron sulphide, 9 to 14 parts; potassium carbonate, 8 parts.

In England the process of refining and restarring the star bowls, also a pot-furnace operation, is as follows: The lumps of metal, when cold, are removed from the mold and are thoroughly cleaned from the adhering skin of slag by chipping with sharp hammers, this part of the work being sometimes done by women. Unless this cleaning process is carefully done, it is well-nigh impossible to obtain good stars on the finished metal. The chippings are returned to the second smelting. Having been cleaned, the star bowls are broken small. The charge made is about 84 lb., together with enough flux to surround the ingots completely; the quantity is generally 8 lb. for ingots of the ordinary shape. The melting takes place in the crucibles standing close to the fireplaces, where the fusion is most rapid. The metal is charged first and is closely watched; as soon as it begins to melt, the flux is added; and as soon as the fusion appears to be complete the furnace man stirs the mixture once round only, with an iron rod, and the charge is then poured out. The flux is used over and over again, being regenerated by the addition of carbonate of potash. The ingots must be completely surrounded by the flux; there must be a thin layer of it between the mold and the metal, and also the whole surface of the ingot must be covered by the flux to a depth of a quarter of an inch. Any traces of the flux still adhering to the ingot are removed by washing in warm water, with the assistance of a little sharp sand.

For a charge of 60 to 70 lb. of bowl metal, with 1 to 2 lb. potash and 10 lb. of slag, obtained from a previous charge of French metal, the time required is three-quarters of an hour.

**Refining in Reverberatory Furnaces.**—The refining operation is in most cases carried on in a small furnace, of reverberatory type, and proceeds about as follows: 1,200 to 1,500 lb. of impure antimony are melted as one charge, to which is added 3 to 7 per cent of soda, mixed with a little coke dust or fine charcoal. The slag from this fusion gradually becomes thicker and thicker, and after about 3 hr. is skimmed off through the working door. Up to this point, the iron and sulphur remain as impurities in the metal. They are next removed by adding ingredients capable of forming antimony glass, such as oxysulphide of antimony. For each 100 lb. of antimony in the charge, 3 lb. of liquated sulphide of antimony and  $1\frac{1}{2}$  lb. of antimony tetroxide are thrown in, and as soon as these are fused,  $4\frac{1}{2}$  lb. of potash are added. Care is taken that the bath of metal is completely covered with the fluxes.

The metal can be ladled out, after another 15 min., being handled cautiously, in order to secure the starred appearance of the ingots. Three charges of about 1,500 lb. each can be refined in one of the small furnaces used, in 24 hr., with a coal consumption of 1,300 lb.

The slag obtained in the final step of the refining operation is called "star slag," and consists principally of antimony glass, carrying from 20 to 60 per cent of antimony. It is used repeatedly for refining, until it becomes too impure for the purpose, when it is charged along with the ore for the first smelting. The other slags obtained in the course of refining are also added to the smelting ore charges.

The proper procedure for charging any of the above mixtures is as follows: The compound, after being thoroughly mixed, is immediately charged into the reduction furnace as soon as the skimming is finished. The doors are closed and vigorous firing is maintained; as soon as it is observed that the mixture is completely melted, ladling commences. Each ladle dips into the molten metal and, in coming out, picks up a certain quantity of the molten couverture, which, when poured out together with the metal into a hot mold, completely covers the metal on all sides. Ladling must be done rapidly for each moldful—four or five ladles to one slab of regulus according to



the size of the ladle used. The thickness of the solidified couverture varies from 1 to 2 mm. on all sides except the top, which varies from 5 to 7 mm. The amount of couverture required for each charge varies from one-sixth to one-fourth the weight of the regulus produced. It is remarkable that generally the weight of the solidified couverture hammered off from the slab after cooling is less than the original weight of the mixture put in by about one-third, due in part to volatilization and in part to wall-fluxing during melting. The couverture can be used over again the second or third time, sometimes with an addition of a little soda, until it is so contaminated with impurities that it cannot produce any good stars. Then the wornout couverture is mixed with the ordinary charge of trioxide or tetroxide and is calculated as an equivalent amount of soda required for that charge. In connection with this, the practice at the Loong Kee and the Pao Tai smelters may be mentioned: The Loong Kee smelter uses for every 14 tons of regulus produced 1.14 tons of couverture which, according to No. XII of the table on page 838, contains 1 ton of trioxide and 0.14 ton of soda. The Pao Tai smelter uses 1 ton of couverture No. XIV for 14.5 tons of regulus.

The refining operation itself is done in (1) pot furnaces, or (2) reverberatory furnaces. In the Herreshmidt method, as used by the Wah Chang Mining & Smelting Co. in China, the refining is practically done in the furnace (Fig. 16), while additional refining and starring are accomplished by means of the starring mixture poured into the molds ready to receive the molten metal. The metal obtained by the smelting processes in vogue in Mexico, England, Hungary, France, and other countries is so impure that refining must be carried out as a separate process.

**Refining in Pot Furnaces.**—This type of refining furnace has been in use at Septèmes in France, in England, and at Oakland, Cal. The Septèmes furnace was 7 ft. long and 5 ft. wide at the middle, with a height of roof above middle of bed of 1 ft. 6 in. It held thirty crucibles, each holding a charge of 48.5 lb. of impure antimony. Crucibles were made of fireclay, and lasted five or six charges. To each charge were added 13 to 17 lb. of flux, which consisted of a mixture of sulphate and carbonate of soda, with a little salt and pure oxidized antimony ores. Fusion lasted 6 hr., with a consumption of 450 to 550 lb. of coal—a low red heat being maintained.

The loss due to volatilization during this reverberatory refining tends to run quite high, in some cases 20 to 30 per cent. The flux dust consists principally of the trioxide and tetroxide, and its retreatment, of course, cuts down the net loss of the process.

The composition of specimens of regulus before refining is shown in the following table:

	English process		Sublimation process	
	Specimen 1, per cent	Specimen 2, per cent	Specimen 1, per cent	Specimen 2, per cent
Sb.....	94 50	84 00	97 20	95 00
Fe.....	3 00	10.00	2.50	4.00
S.....	2 00	5 00	0.20	0.75
As.....	0.25	1.00	0 10	0.25

Typical analyses of refined antimony supplied from the English, Japanese, and Chinese producers are shown in the following figures:<sup>1</sup>

	Cookson's "C," per cent	Hallett's "H," per cent	Japanese "MC," per cent	Chinese, per cent
Lead .....	0 102	0.718	0 424	0.029
Tin .....	Trace	0.012	0 012	None
Arsenic .....	0.092	0.210	0.095	0.090
Bismuth .....	None	None	None	None
Copper .....	0 046	0 046	0 043	0.012
Cadmium .....	None	None	None	None
Iron .....	0 004	0 007	0.007	0.004
Zinc .....	0 034	0.023	0.023	0.027
Nickel } .....	0.028	None	None	Trace
Cobalt } .....				
Sulphur .....	0 086	0 128	0 201	0.078
Antimony (by difference) .....	99 608	98 856	99 195	99.76
Total .....	100	100	100	100

A trade analysis of the Chinese "W.C.C." brand, typical of the highest grade of regulus produced by the Chinese plants, shows:

	PER CENT
Lead .....	Trace
Tin .....	0.030
Arsenic .....	0.095
Bismuth .....	None
Copper .....	Trace
Cadmium .....	None
Iron .....	0.009
Zinc .....	Trace
Nickel } .....	None
Cobalt } .....	
Sulphur .....	0.018
Antimony (by difference) .....	99.848

**Summary of Antimony Metallurgy.**—The only ore of practical importance is the sulphide stibnite of low specific gravity, 4.5. The crushing of stibnite leads to the production of large quantities of fines and slimes, as the mineral is sectile as well as brittle. Methods based on gravity concentration are, therefore, wasteful, and it is true also that they can be dispensed with, in most cases because there is a process available for the direct extraction of the metal from poor, medium, and rich materials, into which classes an ore can be readily graded by hand sorting. The expense of concentration does not appear, so far, to be justified in the case of ores containing no other valuable constituent than antimony, unless it be to save

<sup>1</sup> COWAN, W. A., "The Metallurgy of Tin and Antimony." *Trans., A. I. M. E.*, 17 (1914).

freight. In this case, flotation appears to be by far the most satisfactory method, and it will undoubtedly find a place in antimony metallurgy; it is already contemplated in New Brunswick, as a measure that may bring this field into commercial production, in competition with the Chinese hand-labor product.

Of the processes for extracting antimony, no hydrometallurgical or electrolytic method is beyond the experimental stage. The important smelting processes are subdivided into: (1) roasting to trioxide or tetroxide and reduction of either oxide by carbonaceous fuel; (2) precipitation of metal from crude by iron; (3) stibnite smelting in the blast furnace. It is to be emphasized that, whatever smelting method be followed, an antimony plant must have a particularly good flue and condensing system. Bag houses are used; the Cottrell system was installed by one plant in 1918 and apparently has been entirely successful. The Cottrell oxide is understood to be very white, two forms of oxide being produced; heavy octahedral crystals in the Cottrell and light prismatic crystals in the flues preceding the Cottrell apparatus. As volatilization is heavy in all cases, the success of any antimony plant involves thorough and adequate recovery of the fumes.

In the roasting of stibnite, it is to be noted that the ore may be converted either into the volatile trioxide—the first step in the production of the metal by the French, or Herrenschildt process—or to the non-volatile tetroxide. The latter step has now become almost obsolete. By roasting to the trioxide, the antimony is freed from the gangue and non-volatile metallic matter, and the presence of heavy gangue is useful in this operation in retarding the fusibility of the stibnite. This volatilizing roasting, therefore, affords the best method of utilizing the poorest ores. It is not suitable for rich, fusible, ores.

Roasting to the tetroxide, now in disuse, fails to separate the metal from the gangue, in the case of the poor ores, and is a tedious operation in the case of the richer ores, and one that is unnecessary inasmuch as the latter class can be treated by direct precipitation methods. As to roasting, then, the process for the poorest ores and liquation residues (about 5 to 20 per cent of antimony) is the method involving the trioxide, which is, necessarily, applicable only to ores close at hand, as otherwise freight must be paid on low-grade material. This process is the one used, also, for gold-antimony ores, the precious metal, of course, remaining in the residues.

As the ore becomes higher in grade, roasting becomes increasingly unsatisfactory for the removal of all the antimony from the gangue. Ores carrying 25 to 40 per cent of the metal are in a zone too rich for good roasting and too poor for liquation or precipitation smelting. For ores and products of this antimony tenor the blast furnace offers the method of greatest efficiency, having the advantage of large capacity, and being adaptable to the handling of all kinds of by-products. The blast furnace gives the three products—metal, high-grade fume, and a slag practically free from metal. The blast furnace in an antimony smelter serves as a catch-all for odds and ends. Its one disadvantage—high volatilization—can be controlled by high shaft and ample fume and dust-recovery facilities.

Volatilization and the necessary dilution of the charge, however, stand against the use of the blast furnace for rich ores. Material richer than 45 per cent and below 60 per cent is in a class, then, which is not suitable for roasting or blast furnacing, and still contains too much gangue for best results in direct precipitation smelting. For such ores liquation is considered the best process, being a form of pyroconcentration, which splits medium ores into higher and lower products more conveniently treated than the original ore. These products are: (1) crude, for subsequent smelting by precipitation with iron, and for which there is, also, always a considerable market from the chemical trade; (2) liquation residue, for subsequent treatment by roasting

or blast furnacing, according to its grade; and (3) flue dust, which is worked up for metal, and used in the refining operation.

Lastly, the richest ores (over 60 per cent), and crude, are best smelted by the precipitation process. This proceeds most efficiently in the reverberatory furnace. This class of material has almost no gangue, and requires practically no fluxing. The principle of this precipitation process is simple, but its manipulation is somewhat intricate. The final temperature of the bath must be high, else the iron does not exert its preferential affinity for sulphur over antimony. In one English smeltery, the precipitation process continues to be carried on in crucibles, but this is a very expensive method.

For the reduction of oxidized antimony materials—rich ore, flue dust, and trioxide—by carbon, the reverberatory is the most generally employed and most suitable

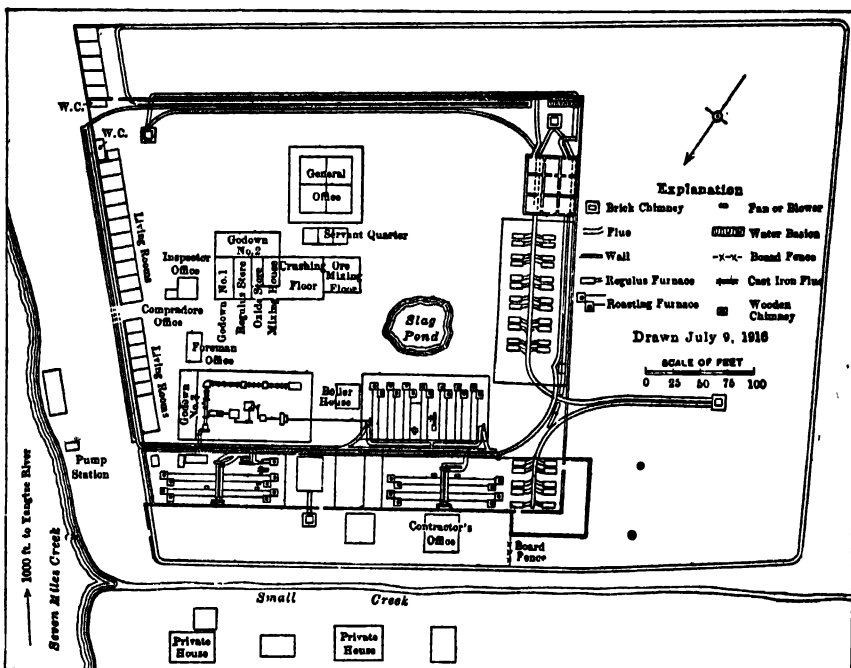


FIG. 19.—Plan of Loong Kee smelter, China.

furnace. In this operation, which forms the second step in the Herrenscheidt process, the sodium salts (sulphate, carbonate, and chloride) are used as fluxes, and also keep down volatilization. The finely ground ore, or flue dust (trioxide) is intimately mixed with, say 10 per cent of powdered charcoal or coke. A high-grade metal is the result of the reduction, which can be "starred" in one operation, after skimming and adding the refining flux. The slag is returned to the reverberatory or blast furnace.

Refining of antimony metal is largely an empirical proceeding, varying in different localities to suit conditions. It has the double object of removing as many of the impurities as possible, and of giving the final metal a good "star"—an artifice called for by the trade but having no bearing, necessarily, on the degree of purity of the regulus. It may be produced with inferior qualities of metal, while the highest grades may show an imperfect star or none at all, if precautions in pouring and cooling are not observed. In refining, iron, if present in considerable amount, is removed

by a fusion with crude or rich ore, the sulphur of which combines with the iron to form a matte that can be skimmed off. Sulphur is removed by adding oxide dust to the refining slag. Lead does not yield to ordinary methods of refining, and it is thus a most objectionable impurity in antimony ore. On a large scale, refining is performed in the reverberatory; in small plants it is done in graphite crucibles.

A typical layout of a reverberatory furnace plant is shown in Fig. 19, a plan of the Loong Kee Smelting Works, the largest of the Chinese plants.

**Control of the World's Antimony Resources.**—The total world's production of antimony during the three years prior to the World War averaged about 30,000 tons. Approximately, 70 per cent of this quantity was supplied by China, in the form of antimony metal, needle or crude, and ore. The United States, France, Germany, and Great Britain normally consume 85 per cent of the antimony of the world, and of these France alone is independent of foreign sources of supply.

The peace-time consumption of antimony is limited rather by the relatively restricted uses to which antimony is put than by any lack of potential supply. As a consequence, steady production has been maintained only from those districts in which operating expenses are low and markets readily available, or in which the deposits contain other metals of value. Modern warfare, however, creates a special use for antimony—in the manufacture of shrapnel—which requires many times the amount of antimony necessary for ordinary peace uses. In each of the three important wars of the last 30 years, the Boer War, the Russo-Japanese War, and the World War, the curves of antimony prices and production have risen sharply in accordance with the demand and have fallen as rapidly after the need for munitions was past.

The antimony-producing countries of the world may be divided into three groups as follows:

1. Principal producing countries in order of importance: China; France and Algeria; Mexico; and Austria-Hungary.

2. Countries in which production is irregular in normal times but in which potential reserves are considerable and production important at high-price levels: Bolivia; Australia (Victoria); Burma; South Africa; Italy; and Spain.

3. Countries in which normal production is small and in which known reserves are probably less important: United States and Alaska; Canada; Peru; Germany; Turkey (Asia Minor); Serbia; Portugal; Borneo; Indo-China; and Japan. Canada, through the activities of the North American Antimony & Smelting Co. near Lake George, New Brunswick, may take a more important place.

Prior to 1914, only one company in the United States had attempted the smelting of antimony. During the war, considerable activity prevailed, however, and several companies undertook the smelting of foreign and domestic ores. China, Bolivia, and Mexico were the principal sources of ore supply. The success of all these enterprises was only temporary, as under normal conditions high cost of production in this country prevents successful competition with Chinese metal. American smelting interests exert little control on the antimony of the world at the present time. The smelter capacity of the country is estimated at 6,000 to 7,000 tons of metal per annum all of which is idle at present.

## CHAPTER XXIV

### BISMUTH

By WALTER C. SMITH<sup>1</sup>

**History.**—The metal bismuth appears to have been unknown to the earlier metallurgical writers. Agricola makes the first mention of it as a form of lead, and describes a method of separation from its associated minerals by liquation. Mathesius, in his "Bergpostilla," 1553–1562, describes it as a white metal, like pyrite.

**Physical Properties.**—Bismuth is a very brittle metal of high luster and a characteristic reddish-white color. It looks much like antimony, but can be distinguished from it by its color. Other physical properties are: atomic weight, 208; number by Moseley's arrangement, 83; hardness, 2 to 2.5; specific gravity in solid phase, 9.82; specific gravity in liquid phase, 10.055; expansion on solidification, 2.35 per cent.; fracture, coarsely crystalline; color, reddish white; luster, brilliant metallic; crystallization, hexagonal rhombohedra; melting point, 267°C. (511°F.); boiling point, 1090 to 1450°C. (1994 to 2642°F.); thermal conductivity, 1.8 per cent of silver; electrical conductivity, 1.19 per cent that of silver at 13.8°C.; specific heat,  $S_m$  (0 to  $t^\circ$ ),  $0.0285 + 0.00002t$  (cal. per kilogram); heat in metal at melting point (solid), 9.0 cal. per kilogram; heat in metal at melting point (liquid), 21.0 cal. per kilogram; latent heat of fusion, 12.0 cal. per kilogram; magnetic properties, most diamagnetic substance known.

**Chemical Properties.**—Bismuth is not affected by air at ordinary temperature; heated in contact with air, it becomes coated with a grayish-black oxide at temperatures just below the melting point; at higher temperatures a yellow or green oxide ( $\text{Bi}_2\text{O}_3$ ) is formed. Bismuth burns with a bluish flame at a bright-red heat, forming  $\text{Bi}_2\text{O}_3$ , which often looks like yellow smoke. Water does not affect bismuth at ordinary temperatures; at white heat, water vapor is slowly decomposed by it.

Bismuth combines directly with chlorine, bromine, and iodine. It is not attacked by dilute sulphuric, dilute hydrochloric, or cold concentrated sulphuric acids; hot concentrated hydrochloric acid attacks bismuth slowly. It dissolves in hot concentrated sulphuric acid and is readily soluble in nitric acid or *aqua regia*, either hot or cold. Molten bismuth combines directly with sulphur to form bismuth sulphide ( $\text{Bi}_2\text{S}_3$ ). Bismuth is precipitated from solution as metal by metals of the alkalis, the alkaline earths, zinc, manganese, iron, nickel, cadmium, copper, tin, and lead. It is precipitated from solution as the sulphide by hydrogen sulphide and all the soluble sulphides. Basic salts of bismuth are precipitated from solutions of the sulphate, nitrate, and chloride of bismuth upon heavy dilution with water.

**Uses.**—Bismuth is a constituent of a number of low-melting-point alloys; it is also added to certain alloys to correct excessive shrinkage upon solidification.

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The composition of some of the common low-melting-point alloys is shown in the following table:

Name	Composition				Melting point, degrees Centigrade
	Bi	Pb	Sn	Cd	
Newton's metal.....	2	5	3	..	94.5
Rose's metal.....	2	1	1	..	93.75
Lichtenberg's metal.....	5	3	2	..	91.60
Wood's metal.....	4	2	1	1	71.0
Lipowitz's metal.....	15	8	4	3	60.0

Bismuth alloys are used for solders; in dental amalgams; for taking impressions of woodcuts, coins, and similar objects; for fusible safety plugs; heads for automatic-sprinkler systems, fusible cores for electroplating and for silvering mirrors. Small quantities of bismuth compounds are used in the ceramic and paint industries. It is extensively used for the preparation of pharmaceutical compounds, for which purpose the subnitrate, the subiodide, the subcarbonate, the oxychloride, and the formic iodide of bismuth are the most widely known. Bismuth used in the manufacture of pharmaceutical compounds must be especially pure, arsenic and tellurium being particularly objectionable.

*Mineral Industry*, 1921, gives the following data:

#### IMPORTS OF BISMUTH INTO THE UNITED STATES

Year	Pounds	Value
1911.....	178,298	\$321,360
1912.....	166,980	305,282
1913.....	151,030	257,176
1914.....	133,190	241,448 <sup>a</sup>
1915.....	34,237	72,587
1916.....	64,821	155,925
1917.....	88,465	196,113
1918.....	85,611	208,098
1919.....	76,539	228,376
1920.....	75,781	97,489
1921....	94,085	114,891

The estimated production of bismuth in the United States is given as follows:

1919.....	290,000 lb.
1920.....	228,000 lb.

**Sources of Bismuth.**—The supply of bismuth is derived from two principal sources: (1) ores mined and treated for their bismuth content; (2) metallurgical products in which bismuth has been concentrated.

Bismuth ores have been found in commercial quantities in parts of Germany, the old Austro-Hungarian Empire, Chile, Peru, Bolivia, Mexico, United States, China, and Australia. Bismuth usually occurs in ores as metallic bismuth, as bismuth oxide ( $\text{Bi}_2\text{O}_3$ ), sometimes mixed with the carbonate and the hydrate, and as the sulphide

( $\text{Bi}_2\text{S}_3$ ). The ores are seldom found pure, and generally contain more or less of the following impurities: lead, tin, copper, silver, gold, arsenic, antimony, selenium, tellurium, tungsten, vanadium, nickel, and cobalt.

Bismuth often occurs in small quantities in various ores which are mined and treated for the recovery of one or more metals other than the bismuth, the bismuth in these ores being concentrated in certain products which then become a source of bismuth. These products are: enriched lead from the Pattinson process of lead refining; litharge; furnaces and cupel bottoms; mattes; speiss; anode slime from electrolytic refining of lead, copper, and tin; and various flue products.

**Extraction of Bismuth.**—Both fire and wet methods, or a combination of both methods, are used for the extraction of bismuth from ores and metallurgical products. The greater portion of the production is obtained by fire methods. Bismuth produced by either method is generally too impure for use, and must be refined. One of the earliest methods to be employed for the recovery of bismuth was liquation.

**Extraction by Liquation.**<sup>1</sup>—This process was formerly used in Saxony. The liquation was carried out in inclined cast-iron pipes, heated with a wood or coal fire. The ore containing metallic bismuth was introduced into the pipes and the readily fusible bismuth melted and flowed out of the lower ends of the pipes, leaving the gangue of the ore as a residue in the pipes. This residue still contained considerable bismuth, and was drawn from the pipes, smelted to a bismuthic speiss, and then retreated in the liquation furnace. One form of liquation furnace carried eleven cast-iron pipes, each 4 ft. long, 10 to 12 in. high, and 6 to 8 in. wide; each pipe received a charge of about 33 lb. of ore; from 15 to 20 min. were required for the liquation, and the furnace consumed approximately 690 cu. ft. of firewood per 24 hr.

**Extraction by Fusion.**—The fusion of raw or roasted bismuth ores, with carbon for reduction and the proper fluxes to yield a fusible slag, has superseded the liquation process. The fusion is carried out either in crucibles or small reverberatory furnaces. Metallic iron is added to the charge to decompose any bismuth-sulphides in the melt. Lime, soda ash, salt cake, fluor spar, and feldspar are some of the fluxes used to give a fusible slag. The products of the fusion are metallic bismuth, matte, or speiss, and slag. The melt is usually cast into molds and the three products separated after solidification. The matte or speiss retains some bismuth and hence is crushed, roasted, and resmelted. Crucibles made of fire clay, and furnace hearths made of fire brick give the best results; the furnace hearth should be removable to permit rapid repairs.

**Extraction of Bismuth from Alloys.**—Alloys of bismuth and lead, or with lead and the precious metals, are often treated for the recovery of the bismuth. When a lead-bismuth alloy is subjected to an oxidizing fusion, the lead is oxidized first, the bismuth beginning to oxidize only when the greater proportion of the lead has been removed. The cupellation of a lead-bismuth alloy can, therefore, be so conducted that the first product is litharge; then a litharge containing bismuth; and then, a heavy black oxide of bismuth, nearly free of lead. The bismuth litharge is generally reduced with carbon to metal, and is returned to the cupel furnace. The black oxide of bismuth is reduced with carbon to crude bismuth. The enriched lead from the Pattinson process of lead refining is usually cupeled and yields litharge, bismuth litharge, and a gold-silver alloy called doré. The bismuth litharge is reduced to metal and again cupeled; these operations are repeated until the bismuth is sufficiently concentrated to permit extraction by wet methods.

**Wet Extraction of Bismuth.**—When bismuth is present in ores and metallurgical products as oxide or carbonate, hydrochloric acid is usually employed to dissolve

<sup>1</sup> SCHWABEL, "Handbook of Metallurgy," vol. 2.



the bismuth. Metallic bismuth or alloys are treated with nitric acid, *aqua regia*, or hot, concentrated, sulphuric acid. The wet method most commonly employed for the extraction of bismuth is conducted approximately as follows: Finely crushed bismuth litharge, cupel bottoms, or other oxidized material, containing from 5 to 20 per cent of bismuth, are treated in stoneware or other suitable vessels with hydrochloric acid. The proportions are 140 to 155 lb. of hydrochloric acid and 22 lb. of water for each 100 lb. of material treated. The mixture is heated gently and stirred for from 5 to 6 hr.; water is carefully added until the white bismuth oxychloride just begins to form; it is allowed to settle for from 6 to 8 hr., and the clear solution is then siphoned into wooden tanks. Water is next added to this solution in order to complete the precipitation of the bismuth oxychloride, and the mixture is again allowed to settle. The clear liquor is siphoned off and is treated with scrap iron to precipitate any copper carried by the solution. The bismuth oxychloride is washed with hot water to remove as much lead chloride as possible; is dissolved in hydrochloric acid; is reprecipitated by dilution with water; and this treatment is continued until the bismuth oxychloride is free of all but the last traces of lead. It is then filtered, dried, and smelted with lime and charcoal to metallic bismuth. The bismuth produced by this method usually contains small amounts of lead, silver, and other impurities. The leach residue contains lead, silver, and other metals; it is washed, filtered, dried, mixed with lime or soda ash, and carbon, reduced to metal, and reworked in the cupel furnace for the recovery of the silver.

Mrazek<sup>1</sup> proposed to treat alloys of lead and bismuth with sulphuric acid. Alloys containing from 50 to 60 per cent bismuth were granulated and treated with hot, concentrated, sulphuric acid. The bismuth and silver dissolved, and the lead remained as an insoluble residue of lead sulphate; the silver was precipitated from the solution by means of sodium chloride, and then the bismuth by means of iron. The spongy bismuth was washed, dried, and melted.

De Luyne<sup>2</sup> proposed to treat alloys of bismuth, lead, and tin as follows: The alloys were to be treated first with cold concentrated hydrochloric acid in order to remove as much of the tin as possible; the residue was then to be treated with *aqua regia*, and the bismuth precipitated from the solution by dilution with water. The bismuth oxychloride was to be reduced with lime and charcoal, or by the reduction with zinc in the presence of hydrochloric acid. De Luyne also proposed to treat lead, tin, and bismuth alloys with nitric acid, the lead and bismuth being soluble and the tin insoluble; the bismuth was to be precipitated from the solution with metallic lead, and the lead as carbonate with sodium carbonate.

**Electrolytic Extraction of Bismuth.**—Borchers proposed to treat alloys of lead and bismuth, and lead-bismuth and silver, by electrolysis of the molten alloy under fused alkaline chlorides in specially designed cells. Under the action of the current, lead is dissolved as chloride and deposited as metallic lead at the cathode; the bismuth and silver do not dissolve and collect at the bottom of the anode compartment. With a current density of 100 amp. per square foot, the voltage drop was reported to be 0.5 volts; or 13.4 lb. of lead can be separated per kilowatt-hour. This process has never been used commercially. Alloys of bismuth and lead have been treated by electrolysis, using the Betts process. The alloy anodes and pure lead cathodes are immersed in an electrolyte of lead fluosilicate and hydrofluosilicic acid; a current density of from 15 to 20 amp. per square foot of cathode is employed; pure lead is deposited on the cathode; the bismuth remains on the anode as a hard porous cake, which has to be broken off, washed, and melted down to a bismuth carrying from 3 to 10 per cent of lead.

**Recovery of Bismuth from Lead Bullion.**—Three methods are available for the desilverizing and refining of lead bullion; these are the Parkes process (zinc-

<sup>1</sup> Oesterr. Zeit., 84 and 85 (1874).

<sup>2</sup> Dinglers polytech. J., 187, 289.

ing); Pattinson process (crystallizing), or one of its several modifications; and the electrolytic process.

The Parkes process does not remove the bismuth from lead bullion, and, therefore, is not satisfactory for treating a bismuth-bearing bullion. The Pattinson process yields two products: a refined lead, more or less free of bismuth; and an impure lead, called work lead, which contains the major portion of the bismuth, silver, and gold contained in the original bullion. This work lead is generally cupelled to recover the gold and silver, and the bismuth is concentrated in the bismuth litharge from which the bismuth is extracted. The electrolytic process yields a high grade of refined lead, even from bullion carrying a relatively large amount of bismuth, and an anode slime or sludge. This anode slime is treated for the recovery of the gold, silver, bismuth, and other elements of commercial value. An American refinery at one time treated all of its lead bullion by the Parkes process for the recovery of gold and silver. The desilverized bullion was rich in bismuth and was then treated in a modified form of the Pattinson process, yielding corroding lead and an enriched lead. This enriched lead was cast as anodes, and sent to the electrolytic tanks for refining by means of the Betts process. The anode slime was then treated for the recovery of the bismuth.

**Recovery of Bismuth from Electrolytic Lead Slime.**—The slime is removed from the scrap anodes, washed to remove soluble lead and acid, filtered, dried, and melted in a reverberatory furnace. The lead, antimony, and arsenic are then separated from the gold, silver, copper, tellurium, and bismuth by means of a very carefully controlled oxidation. This operation can be so conducted as to force all of the lead, arsenic, and antimony into an oxide slag carrying only traces of bismuth, leaving the gold, silver, copper, tellurium, and bismuth as a metal. This metal is transferred to a second furnace and the oxidation continued until practically all of the bismuth, copper, and tellurium have been removed as molten oxides, and a gold-silver doré results. The oxide slag of bismuth, copper, and tellurium is crushed to small size, mixed with salt cake and coke breeze, or soft coal, and smelted in a small reverberatory furnace to an impure bismuth, matte, and soda slag. The matte and slag are skimmed off and the bismuth cast as bars for refining; the matte and soda slag are then reworked for the recovery of the bismuth and other metals which they still contain.

**Refining of Bismuth.**—Bismuth produced by fire methods usually contains lead, arsenic, antimony, sulphur, selenium, tellurium, iron, gold, silver, and sometimes nickel and cobalt as impurities. The following are analyses of four samples of crude bismuth:

	Peru <sup>1</sup>	Australia <sup>1</sup>	United States <sup>2</sup>	United States <sup>2</sup>
Bismuth.....	93.37	94.10	90.45	95.03
Antimony.....	4.57	2.62	0.91	Trace
Arsenic.....	....	0.29	0.26	Trace
Copper.....	2.06	1.94	3.71	2.97
Lead.....	....	....	1.32	0.87
Sulphur.....	....	0.43	0.99	0.21
Tellurium.....	....	....	1.31	0.45
Silver, ounces per ton.....	....	....	154.5	120.2
Gold, ounces per ton.....	....	....	31.6	35.92

<sup>1</sup> *Mineral Ind.* (1895), 72.

<sup>2</sup> Personal Notes.

Impure bismuth is not suitable for many purposes for which the metal is employed and, therefore, must be refined. Refining of crude bismuth can be carried out by three methods: wet, fire, and electrolytic, or by a combination of several of these methods.

**Refining Processes.**—Refining of bismuth by wet methods is seldom used except when the bismuth has been separated by wet methods, or when small quantities of exceedingly pure metal are required. Wet methods are much more expensive than fire methods of refining and cannot be operated on so large a scale.

Liquation of bismuth on cast-iron hearths is practiced to some extent in Saxony for refining of bismuth. The liquated metal is allowed to cool to the freezing point before casting in order to separate any sulphide of bismuth from the metal. The residues remaining on the hearth contain most of the impurities carried by the original bismuth. Lead and tin are not separated from bismuth by liquation, and the liquated metal is seldom suitable for pharmaceutical use.

The refining of bismuth by melting with fluxes gives better results than liquation, but it is often necessary to make several melts, using different fluxes. The choice of flux depends upon the impurities to be removed. The melting of bismuth with fluxes is carried on in crucibles, kettles, or small reverberatory furnaces. Borchers suggests a fusion in cast-iron pots with bismuth oxychloride, sodium chloride, potassium chloride, and caustic soda for the removal of lead. Quesneville claims that a fusion with niter and sodium chloride will remove arsenic, and some lead and iron from bismuth. Werther claims that arsenic may be removed by means of a fusion with one-eighth of its weight of sodium carbonate and one-sixtyfourth of sulphur. Thürach states that arsenic and iron can be removed by fusing bismuth with potassium chlorate to which 2 to 5 per cent of sodium carbonate has been added. Both Méhu and Matthey<sup>1</sup> claim that heating bismuth for a considerable time at a temperature of 395°C. in contact with air will remove the arsenic completely, without the loss of bismuth. Smith<sup>2</sup> removes arsenic, tellurium, and zinc by fusion under a cover of caustic soda, stirring by means of superheated steam. Tamm used thin sheet iron and a cover of borax, at a bright-red heat, to remove arsenic. Johnson, Matthey & Co.<sup>3</sup> treats bismuth containing antimony by heating the metal to the oxidation temperature of antimony, and poling with wood. An example is: 700 lb. of bismuth (96.2 per cent Bi, 0.8 per cent Sb, 0.4 per cent Fe, 2.1 per cent Pb, 0.5 per cent Cu, and a trace of arsenic) are heated to 458°C. and poled with wood for 4 hr. The antimony is all removed as a scum or dross. This dross carried 30 per cent antimony and about 10 per cent bismuth. Fusion of bismuth with bismuthic oxide will remove both arsenic and antimony from the bismuth. The amount of oxide used is from two-and-a-half to three times the weight of antimony in the crude bismuth. Borchers<sup>3</sup> treated crude bismuth by a fusion with caustic soda, sodium and potassium chlorides, and bismuth oxychloride to remove lead; then by a fusion with caustic soda and niter to remove antimony. Tamm used a mixture of 8 parts of potassium cyanide and 3 parts of sulphur added to the molten metal for the removal of copper as copper sulphide. This treatment also removed some of the lead, arsenic, antimony, and tellurium. A fusion of crude bismuth with bismuth sulphide is an effective means of removing copper; the same result is obtained by adding sulphur to molten bismuth and stirring with steam. The fusion of bismuth with sodium sulphide gives a good elimination of copper if the melt is properly stirred. Johnson, Matthey & Co.<sup>4</sup> employs crystallization similar to

<sup>1</sup> MATTHEY, *Chem. News* (1893), 63 to 67.

<sup>2</sup> SMITH, W. C., U. S. patent, 1166721, Jan. 4, 1916.

<sup>3</sup> *Electro-metallurgie* (1895), 328; (1903), 481.

<sup>4</sup> *Proc. Roy. Soc. (London)*, 42, 89 to 94.

the Pattinson process for lead as a means of separating lead from bismuth, the lead tending to concentrate in the liquid portion and the bismuth in the crystals. Examples follow:

	PER CENT LEAD
Original bismuth carried.....	14.6
First crystallization gave crystals carrying.....	9.8
Second crystallization gave crystals carrying.....	5.1
Third crystallization gave crystals carrying .....	3.8
Fourth crystallization gave crystals carrying.....	2.5
Fifth crystallization gave crystals carrying .....	0.4

Starting with 10,675 lb. of leady bismuth carrying 5 per cent lead, six or seven crystallizations yielded 9,306 lb. of good commercial bismuth, or a return of 94 per cent of the total bismuth; and 1,188 lb. of alloy, carrying 40 per cent lead. The crystallization can be carried on, if necessary, until complete elimination of the lead is obtained. Gold and silver<sup>1</sup> can be separated from bismuth by crystallization, as in the Pattinson process for lead. Example of the separation of gold and silver from bismuth by crystallization:<sup>2</sup>

	Gold, ounces per ton	Silver, ounces per ton	Lead, per cent
Original metal.....	1.09	52.6	0.053
Metal from first crystals.....	0.49	21.8	0.025
Metal from second crystals.....	0.23	11.3	0.011
Metal from third crystals.....	0.112	5.0	0.005
Metal from fourth crystals.....	0.005	2.4	Trace
Liquid from first crystallization.....	2.21	106.3	0.112
Liquid from second crystallization.....	1.05	49.8	0.050
Liquid from third crystallization.....	0.55	21.3	0.026
Liquid from fourth crystallization.....	0.24	12.0	0.011

Approximately two-thirds of the metal was removed as crystals in each crystallization.

Gold and silver can be removed from bismuth by zincing, as in the Parkes process for lead refining.<sup>3</sup> The operation is carried out as follows: the crude bismuth is melted and about 2 per cent of zinc is added, and the temperature raised to a dull-red heat and stirred well. The mixture is then allowed to cool until a slight crust forms. This crust is then skimmed off and zinc added a second time, the temperature is raised, and the mixture is stirred, cooled, and skimmed. From two to three zincings are required to remove the gold; and if the silver in the crude bismuth is high, as many as five or six zincings are necessary to remove it entirely. The zinc skims, consisting of bismuth, gold, silver, zinc, and zinc oxide, are treated for the recovery of the gold, silver, and bismuth. For example: 9,483 lb. of bismuth, with 1 per cent of impurity and 12.5 oz. of gold per ton, were treated, yielding about 9,000 lb. of gold-free bismuth, and 658 lb. of skimmings which contained all of the gold. These skimmings were treated with nitric acid, dissolving the greater part of the bismuth and what little copper was present, care being taken to leave a small amount of bismuth

<sup>1</sup> *Proc. Roy. Soc. (London)*, 42, 89 to 94.

<sup>2</sup> *Personal Notes.*

<sup>3</sup> *Op. cit.*, *Proc. Roy. Soc. (London)*, 42, 89 to 94.

oxide with the gold in order to refine it from impurities while melting the gold. The bismuth dissolved by the nitric acid was precipitated and recovered.

Smith<sup>1</sup> treats impure bismuth as follows: Sulphur is added to the molten metal, preferable with steam agitation, until a test shows that the sample of metal is reasonably free of copper. The melt is then allowed to cool to a temperature of 515 to 520°C.; the sulphides are skimmed off and the bismuth cast as bars. The sulphur treatment removes nearly all of the copper, some of the silver (if the latter is very high in the original metal), tellurium, lead, antimony, arsenic, selenium, and zinc. The bismuth from the sulphur treatment is melted in a cast-steel kettle and covered with molten caustic soda; agitation with superheated steam improves the speed of this operation. The caustic soda treatment removes tellurium, selenium, arsenic, antimony, zinc, tin, and sulphur. The metal is then given two to four treatments with zinc, the number of the zincings depending upon the silver in the metal; these treatments are repeated until the gold has been reduced to less than 0.5 oz. per ton, and the silver to less than 50 oz. per ton. The zinc remaining in the metal is then removed with a caustic soda and steam treatment. The clean metal should now contain but small amounts of gold, silver, and lead, and these are removed by several crystallizations. The final crystals are melted and treated with caustic soda until the very last traces of arsenic and tellurium have been removed. No trouble is experienced in producing a metal which will assay 99.95 per cent, or better, in bismuth. It is also stated that sulphur and tellurium can be removed by heating with calcium or magnesium chloride.<sup>2</sup>

**Electrolytic Refining of Bismuth.**—Zahorski<sup>3</sup> proposed to refine commercial bismuth anodes, cast as plates, using carbon or platinum cathodes and an electrolyte of dilute nitric acid. The current density was from 15 to 30 amp. per square foot. Pure bismuth, deposited at the cathode, was collected, washed with dilute nitric acid (to prevent the formation of basic salts of bismuth), dried, and melted down. Lead gradually concentrates in the electrolyte, which, therefore, has to be renewed from time to time. This process has never been used commercially.

Whitehead<sup>4</sup> developed a method of electrolytic refining of bismuth which has had considerable application in the United States. He uses a shallow earthenware cell similar to that used in the Balbach-Thum silver parting process. Sheet lead, which covers the entire bottom of the cell, acts as the cathode. The anodes are carried in a wooden basket lined with a layer of heavy cotton duck. Each anode carries its own electrical connection, cast as a part of the anode, and four anodes are used per cell. The electrolyte consists of bismuth chloride solution and considerable free hydrochloric acid. The current density is from 15 to 25 amp. per square foot of active cathode surface. The bismuth deposits on the cathode as a series of rough nodules which often resemble flowers in form, and this deposit has to be broken down every 8 to 10 hr. to prevent short circuits. The cells are dismantled every third to fourth day; the bismuth removed; washed with dilute hydrochloric acid; drained and melted under caustic soda in a cast-steel kettle; and cast as refined bismuth. Bismuth refined by this process usually carries 15 to 30 oz. of silver per ton, and traces of gold, lead, and tellurium, if these elements are present in the anode metal. The caustic treatment during the melting of the cathode deposit removes the tellurium, and one or two crystallizations remove the gold, silver, and lead; the liquid metal from the crystallizations is usually cast as anodes and rerun in the cells. The anode slime is collected, washed with dilute hydrochloric acid, mixed with sodium carbonate, and treated for the recovery of the gold, silver, and bismuth contained.

<sup>1</sup> *Op. cit.*, U. S. patent 1166721.

<sup>2</sup> DARLING, U. S. patent, 1318335.

<sup>3</sup> "Mineral Industry," p. 72 (1893).

<sup>4</sup> Personal notes.

**General Notes.**—Reverberatory furnaces used for handling bismuth-bearing products should be built inside of a water-tight metal pan to prevent the leakage of the low-melting-point alloys which tend to form, and which, under some conditions, will penetrate as much as 10 ft. of earth beneath the furnace if allowed to escape from the furnace. The property of bismuth to expand upon solidification causes trouble in reverberatory furnaces handling bismuth-bearing products. The bismuth, or its alloys, works under the furnace bottom, and each time the furnace is cooled below the freezing point of the alloy the action is similar to that of a hydraulic jack; something has to give way, and it is generally the furnace bottom. The best preventive for this condition is to keep the temperature of the furnace bottom above the freezing point of the alloy at all times, making repairs to the hot furnace.

Metallic bismuth is not particularly volatile, but bismuth oxide is quite volatile. All operations in which bismuth, in the form of the oxide, is subjected to temperatures of more than a red heat are apt to cause a serious loss of bismuth as fume, unless some efficient fume-collection apparatus has been provided. Filtration through cotton or woolen bags, the Cottrell process of electrical precipitation, and some of the more efficient types of dust washers have been used for this work. The collected fume is usually a mixture of several oxides and has to be smelted to an impure lead bullion, which is then reworked for the metals contained.

## CHAPTER XXV

### LEAD

By G. C. RIDDELL<sup>1</sup>

**Nature and Uses.**—Lead is the heaviest and the softest of all the common metals. It has a specific gravity of 10.37 to 10.65 (molten), 11.35 to 11.37 (solid); it is, in its pure metallic state, so soft as to be readily scratched by the finger nail, while it easily marks paper with a gray streak. Only the pure metal exhibits this degree of softness, the commercial article containing small amounts of antimony, arsenic, copper, and zinc, being distinctly harder. The degree of hardness increases with the amount of impurity present. The metal has a dull, bluish-gray color, is malleable but not ductile, and of low tenacity. Tensile strength is low, 2,600 to 3,300 lb. per square inch; elastic limit is 0.5 lb. Compressive strength is about two and a half times the tenacity. It is not sufficiently ductile to be drawn into fine wire.

Lead melts at 327.4°C., boils at about 1525°C. (at 760 mm.), but does not readily distill. If, however, a mixture of zinc and lead be subjected to distillation at a high temperature, the zinc vapor carries over with it a considerable quantity of lead vapor; hence the source of part of the losses in lead smelting. Lead is somewhat volatile when heated to a cherry red with access of air.

The market grades are (1) desilverized, (2) soft, and (3) antimonial lead. The terms used to distinguish between classes (1) and (2) are inexact, since the impurities that make lead hard have been removed from desilverized lead in the refining process. The term is retained to distinguish between metal derived from ores containing silver and that from ores that do not. Antimonial lead, an alloy of antimony and lead, is an entirely different product and has become important more as a source of antimony than because of its lead content. It is a by-product of the refining of lead, containing from 15 to 30 per cent antimony.

Lead is used: (1) in the form of the metal, (2) of alloys with other metals, and (3) of various chemical compounds.

As metal, its chief uses are as pipe for conveying water and corrosive solutions; for the protective covering of electrical cables; as sheet lead for lining chambers for the manufacture of sulphuric acid and vats for use in chemical manufacturing processes. Soft lead is required for these uses. In smelting, lead is used as a collector of other metals, particularly of gold and silver, from which it is later separated, now most generally by the use of zinc in the Parkes process of desilverization.

Lead alloys readily with nearly all other metals in all proportions. Its alloys of industrial importance comprise type metal, bearing or babbitt metals, shot, solders, casting metals, some brasses, and the fusible alloys used for the protection of electrical apparatus and in automatic sprinklers for the protection of buildings against fire. Type metal, originally composed of 83 per cent lead and 17 per cent antimony, now often contains bismuth and sometimes a little copper and iron. The alloy of lead, 2 antimony, and 2 bismuth is used for stereotype plates. Less than 2 per cent of arsenic

<sup>1</sup> 1 Broadway, New York, N. Y.

is added to lead used to make shot to increase the hardness and sphericity of the product. Antimony imparts the quality of hardness essential to shrapnel, etc., and the property of expansion on solidification, essential to type metal and casting materials generally. Bearing metals comprise alloys of lead and antimony or these together with copper, tin, and zinc. Lead makes a brass which is soft and machines easily. Solder is commonly an alloy of lead and tin. The melting point varies with the proportions of these constituents and others, sometimes added for special purposes. The cheapest solder in general use is 30 per cent tin and 70 per cent lead. The alloy of 1 part tin and 3 parts lead melts at 452°F., tin alone melting at 442°F. With increase of tin content to 56 per cent the fusion point lowers to 345°F., then rises to 352°F., with further increase to 75 per cent tin. In practice, therefore, solders seldom contain more than 50 per cent tin. The addition of bismuth, cadmium, or mercury lowers the melting below the boiling point of water. Lead fuses can thus be obtained which interrupt electric circuits at any desired temperature.

An electrolytic hard lead alloy was brought out during the World War, known as Frary metal, a mixture of lead with small amounts of the alkaline earth metals, calcium, and barium. This ternary alloy, although it contains barium up to only 2 per cent and calcium less than 1 per cent—the remainder being lead—has remarkable qualities as hard lead. It has a large field of usefulness as a bearing metal, and is particularly popular in trolley-car service. It replaces not only lead-base but also tin-base babbit metals, and to some extent bearing bronzes. It has strength without brittleness, and remarkable antifrictional properties, retaining largely the characteristics of lead in respect to plasticity and unctuousness.

Compositions of some of the leading industrial lead alloys are as follows:

Name	Pb	Sb	Sn	
Type metal:				
Best.....	50	25	25	Cu, 2.
German.....	75	23	2	
Common.....	70	18	10	
French.....	60	30	10	
Linotype (American).....	55	30	15	
Bullets (Shrapnel).....	85	12	3	
Engraving plate.....	94	6		
Pewter:	60	40		
Usual.....	20	80		
French.....	18	82		
Bearing metal:				
Atlantic Coast Line.....	85	15		
Pennsylvania R. R.....	87	13		
Baltimore & Ohio R.R.:				
Thin linings.....	94-96	3-5	0.5-1.5	
Thick linings.....	86	10-12	3-5	
Chicago & Eastern R. R.....	84-85	12-14	2	
Chesapeake & Ohio R.R.....	91.5	7	1.5	
Magnolia metal.....	79.75	15	5	Bi, 0.25



in several quarters that the two other metals—antimony and copper, up to 0.1 per cent content—increase the resistance to the acid.

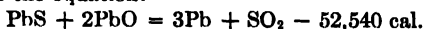
The compounds of lead are poisonous practically in proportion to their solubility; the metal itself and its sulphide, being incapable of absorption as such into the system, are almost innocuous, while the soluble salts, chloride, nitrate, acetate, etc., are active irritant poisons. The oxide, sulphate, and carbonate are less active, but continued exposure to lead fumes, or to any atmosphere in which these substances are present in form of dust, brings on the familiar lead poisoning, or "plumbism," encountered among workmen in the lead-smelting plants. The early symptom of "lead colic" is followed, if exposure to the dust is continued, by "lead palsy," accompanied by emaciation, with the deposit of lead sulphide in the joints and the gums.

**Lead Compounds.**—The more important compounds of lead, and the chemical reactions that are of importance in the extraction of the metal, are as follows:

**Lead Oxide (PbO).**—This is the oxide of greatest metallurgical importance. It occurs in two forms—massicot and litharge. Massicot is an amorphous yellow powder produced by heating lead on a flat hearth at a dull-red heat, continually removing the film of suboxide, and oxidizing it to the yellow oxide at a low temperature, avoiding fusion. On raising the temperature to a bright-red heat this oxide melts, and, on cooling, solidifies as crystalline litharge. Litharge is obtained on a commercial scale by cupeling argentiferous lead. The melting point of litharge is 883°C.; it is volatile in air below 900°C. It is a good conductor of electricity when molten.

Toward acid furnace materials, litharge is a strong base, quickly corroding them by forming silicate. It is an excellent flux, forming fusible compounds with oxides that are infusible alone, such as CaO, BaO, MgO, and Al<sub>2</sub>O<sub>3</sub>. These bases do not always enter into chemical combinations with PbO, but are simply held in igneous solution by an excess of litharge. In the metallic oxide (CuO), 1 part of CuO forms a fusible mixture with 1.8 parts of PbO. No chemical compound occurs, but there is a eutectic with 32 per cent CuO, freezing at 689°C. This explains the fact that, in cupeling, coppery litharge flows more readily than litharge free from Cu. Litharge readily gives up its oxygen. \*S, Te, As, Sb, Sn, Bi, Cu, Zn, and Fe are wholly or partly oxidized when melted with litharge, their oxides being either volatilized or slagged by the surplus of litharge.

Reduction of PbO by carbon begins at 400 to 500° and is vigorous at 700°C. Reduction by carbon monoxide begins at 160°; by hydrogen at 235°C. Heated to bright redness with lead sulphide, in the proportion of 2 molecules litharge to 1 of sulphide, all the lead in both compounds is reduced to metal, and sulphur dioxide evolved, according to the equation:



**Minium, or Red Lead (Pb<sub>3</sub>O<sub>4</sub>).**—This is a combination of 2PbO and PbO<sub>2</sub>, a bright-red powder prepared by heating a mixture of PbO<sub>2</sub> and PbO, at about 250°C.,

$$2\text{PbO} + \text{PbO}_2 = \text{Pb}_3\text{O}_4.$$

**Lead Peroxide (PbO<sub>2</sub>).**—This is a powerful oxidizing agent, detonating with phosphorus. It is used in manufacture of lucifer matches, and in storage batteries, in which latter it is alternately destroyed and reformed during the operations of discharging and recharging.

**Lead Carbonate (PbCO<sub>3</sub>) and White Lead (2PbCO<sub>3</sub> + PbH<sub>2</sub>O<sub>2</sub>).**—Lead carbonate occurs in nature as cerussite. At 200°C. it decomposes into PbO and CO<sub>2</sub>, and at the same temperature is reduced to metallic lead by CO. The white lead of commerce is a hydrated basic carbonate. This pigment, the form in which the greatest use of lead

occurs, is ordinarily prepared by the "Dutch" or "corroding" process, which, briefly stated, consists in the slow corrosion of lead by the vapor of acetic acid, and the conversion of the corroded material into hydrated carbonate of lead by means of  $\text{CO}_2$  generated from decomposing organic matter. The process is tedious, taking over 90 days to complete. The lead is cast into "buckles," which, exposing maximum surface to corrosion, are placed in clay pots containing dilute acetic acid or vinegar. The pots are stacked in tiers and covered with tan bark. The carbon dioxide required for the ultimate conversion of the corroded lead is generated by the fermentation of the bark. The white carbonate is cleaned from the buckles in revolving drums, and the impurities separated by flotation, before it is dried and packed for shipment, or ground in oil for use. From 125 to 129 lb. of white lead should be obtained from 100 lb. of metal.

In another group of white-lead processes—so-called quick processes—finely powdered (atomized) lead is treated with acetic acid and carbon dioxide in revolving drums. In the "mild process" the finely powdered lead is suspended in water, into which air is blown. Basic hydroxide of lead is thus formed, which is later converted partially to basic carbonate by blowing in carbon dioxide. Stringent regulations and restrictions are in force in various countries, on the manufacture of white lead, because of the attendant danger of lead poisoning.

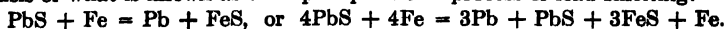
The manufacture of dry white lead, as well as its use except in oil, was forbidden in France in 1915. When proper precautions to control flying dust are taken, however, there is no necessity of lead poisoning at white-lead plants. In some factories, the workmen are required to drink water that contains a little potassium iodide, which acts as a preventive of poisoning.

*Sublimed White Lead (Basic Lead Sulphate).*—This pigment, composed approximately of 75 per cent  $\text{PbSO}_4$ , 20 per cent  $\text{PbO}$ , and 5 per cent  $\text{ZnO}$ , is produced directly from lead ore, whereas the basic carbonate (white lead) is made almost exclusively from lead metal. It is the only white pigment that contains any appreciable amounts of lead oxide. Basic lead sulphate is used extensively in paints, and in the manufacture of oilcloth, stained paper, and rubber goods. The raw material is silver-free galena from the Missouri fields. This is ground fine, mixed with carbon (and gray slag from the ore hearth), and smelted in the oxidizing atmosphere of a slag-eye furnace. The pigment is collected in bag houses. This is known as the Lewis & Bartlett, or sublimed-lead, process, in use at Joplin, Mo. (Eagle-Picher Lead Co.); Alton, Ill. (St. Louis Smelting & Refining Co.); and Bristol, England (Bristol Sublimed Lead Co.). Blue fume, or "sublimed blue lead," is a by-product of the process, and is used in the same industries as is the major product. Sublimed blue lead consists of 50 to 53 per cent  $\text{PbSO}_4$ , 41 to 38 per cent  $\text{PbO}$ , with small proportions of  $\text{PbS}$ ,  $\text{PbSO}_3$ ,  $\text{ZnO}$ , and C.

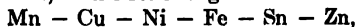
*Lead Silicates.*—Lead silicates are much used for glazing tiles, pottery, etc. Lead oxide and silica begin to combine at the softening temperature of the oxide, i.e., below  $800^\circ\text{C}$ . The silicates do not give up their lead readily, the ordinary reducing agents, sulphur and carbon, decomposing them with difficulty unless the carbon be associated with the liberated silica. Iron in excess effects decomposition of lead silicates at bright-red heat, forming monosilicate ( $2\text{FeO} \cdot \text{SiO}_2$ ).  $\text{FeS}$  throws down some Pb, a double silicate of lead and iron being the result.

*Lead Sulphide (PbS).*—This occurs in nature, as galena, and can be artificially prepared by melting sulphur and lead, or by adding sulphureted hydrogen to a solution of a lead salt. It is produced in smelting lead ores as a sublimate on the cooler parts of the furnace walls.  $\text{PbS}$  melts at about  $1120^\circ\text{C}$ . to a thin fluid which penetrates the fire brick of the furnace; furnace linings usually contain a network of crystalline galena. It volatilizes at temperatures below its melting point. Sublimed galena constitutes the major portion of the accretions on the shaft-walls of lead blast furnaces.

Being isomorphous with  $\text{Ag}_2\text{S}$ ,  $\text{Cu}_2\text{S}$ ,  $\text{ZnS}$ ,  $\text{FeS}$ , etc., lead sulphide readily mixes with these sulphides in all proportions, forming the mattes obtained in smelting complex sulphide ores. Galena is decomposed by fusion with iron, the reaction forming the basis of what is known as the "precipitation" process of lead smelting:



Lead sulphide is decomposed by those metallic elements which have a stronger affinity for sulphur than lead, in the following order:



manganese forming the strongest and lead the weakest sulphide. In the smelting of lead ores, manganese does not have to be considered in this connection, as it is usually present as  $\text{MnO}_2$ , which enters the slag and hence is found only in small amount in the matte.

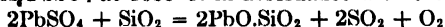
In smelting practice, the decomposition of  $\text{PbS}$  is never complete. It is customary to figure the iron necessary for the decomposition of  $\text{PbS}$  in accordance with the formula  $(\text{Fe} + \text{PbS} = \text{Pb} + \text{FeS})$ ; if less iron is added, the resulting matte remains too rich in lead, while if an excess is supplied it simply goes into solution in the  $\text{PbS}$ - $\text{FeS}$  matte. An excess of iron in the charge, while often advantageous in cutting out crucible crusts, may be disadvantageous in decomposing argentiferous galena, since, due to the affinity of  $\text{Ag}_2\text{S}$  and  $\text{FeS}$ , more silver will be drawn into the matte than can be accounted for by the amount of lead present. In addition to having the correct amount of iron present to decompose  $\text{PbS}$ , it is important to have the temperature as high as possible, within reasonable limits.

A basic ferrous silicate ( $4\text{FeO} \cdot \text{SiO}_2$ ) will decompose  $\text{PbS}$  readily; the single silicate ( $2\text{FeO} \cdot \text{SiO}_2$ ) has little effect.  $\text{CaO}$  and  $\text{BaO}$  have, in the presence of carbon, a decomposing action on  $\text{PbS}$ :



*Lead Sulphate* ( $\text{PbSO}_4$ ).—This occurs in nature as anglesite, and is formed in roasting  $\text{PbS}$  and in precipitating lead salts with  $\text{H}_2\text{SO}_4$ . It is the most stable of all sulphates of the heavy metals, remaining unaltered at a bright-red heat. At  $800^\circ\text{C}$ ., it dissociates, fusion also occurring between  $950$  and  $1000^\circ\text{C}$ ..

Silica decomposes  $\text{PbSO}_4$  at  $1030^\circ\text{C}$ . in accordance with the equation

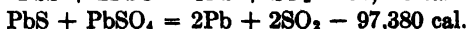
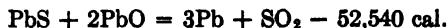


this reaction being the basis of "slag roasting." This decomposition by silica is governed by the viscosity of the lead silicates formed, the viscous slag enveloping  $\text{PbSO}_4$  and blocking the action. According to Mostowitsch the most rapid decomposition and the lowest loss of lead by volatilization lies between the singulo- and bisilicate containing 10 to 15 per cent  $\text{SiO}_2$ .<sup>1</sup>

$\text{Fe}_2\text{O}_3$  also has a decomposing effect on  $\text{PbSO}_4$ , though in less degree than  $\text{SiO}_2$ .  $\text{FeO}$ , above  $800^\circ\text{C}$ ., is oxidized by some of the O from  $\text{PbSO}_4$ . Iron at high temperature is both oxidized and sulphurized:  $4\text{Fe} + \text{PbSO}_4 = \text{Fe}_2\text{O}_3 + \text{FeS} + \text{Pb}$ ; calcium is sulphatized:  $\text{CaO} + \text{PbSO}_4 = \text{CaSO}_4 + \text{PbO}$ ; and metallic lead is oxidized:  $\text{Pb} + \text{PbSO}_4 = 2\text{PbO} + \text{SO}_2$ .

Carbon and carbon monoxide reduce lead sulphate to  $\text{PbS}$ , with the formation, also, of  $\text{Pb}$  and  $\text{SO}_2$  as well as  $\text{PbS}$ . This double reaction explains the disappearance of S as  $\text{SO}_2$  in the reducing fusion of a lead blast furnace. In smelting the gray slag from the ore hearth, as much as 50 per cent of the sulphur is usually expelled.

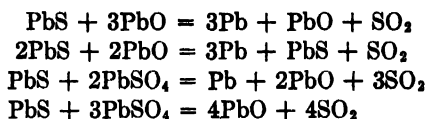
**Reactions between Lead Oxide, Sulphide, and Sulphate.**—Intimate mixtures of  $\text{PbS}$  and  $\text{PbO}$ , and of  $\text{PbS}$  and  $\text{PbSO}_4$ , such as exist in the roasting and smelting of lead ores, react in accordance with the following equations to form metallic lead and  $\text{SO}_2$ :



<sup>1</sup> Horn, H. O., "Metallurgy of Lead," p. 46, McGraw-Hill Book Company, Inc., 1918.

These two equations form the basis of the roasting and reaction or air-reduction process. Except for the fact that the gaseous product  $\text{SO}_2$  is withdrawn from the furnace as fast as formed, both these reactions would reverse and equilibrium result.

If there is an excess of  $\text{PbS}$  or  $\text{PbO}$  over that called for by the equation, the excess remains unaltered. If there is an excess of  $\text{PbSO}_4$ , part or all of the lead is obtained as  $\text{PbO}$ :



*Plumbites and Plumbates.*—The oxides  $\text{PbO}$  and  $\text{PbO}_2$  form plumbites and plumbates with alkali, alkaline earths, and some metallic oxides. The orthoplumbate ( $\text{Ca}_2\text{PbO}_4$ ), occurs in the blast roasting of lead sulphides with lime diluents.

*Lead Ferrite.*—The fact that in the crucible assay for lead the presence of  $\text{Fe}_2\text{O}_3$  acts unfavorably upon the yields of lead is believed due, in part at least, to the formation of ferrite compounds, one of these having the formula  $\text{PbO} \cdot \text{FeO} \cdot 4\text{Fe}_2\text{O}_3$ . The melting point of  $\text{PbO}$  is lowered  $133^\circ\text{C}$ . by the addition of 12 per cent by weight of  $\text{Fe}_2\text{O}_3$ .

*Lead Chloride.*—This is formed by the action of chloride upon lead, and in a chloridizing roast of lead and its compounds. The volatility of  $\text{PbCl}_2$  is the basis of a process for the extraction of lead from its ores, the chloride volatilization process, in which the metallic fume is precipitated by being passed through a Cottrell electrostatic apparatus. The solubility of  $\text{PbCl}_2$  in saturated sodium chloride liquor is also the basis of another process of lead recovery, the brine-leaching process, in which sulphide ores roasted in contact with sodium chloride are dissolved by strong brine solutions, out of which the lead is precipitated either electrolytically or on scrap and sponge iron.

*Lead Selenide and Telluride* ( $\text{PbSe}$  and  $\text{PbTe}$ ).—These occur as clausthalite and altaite, and are formed by the direct union of components. They are readily sublimed, and decomposed by roasting. Selenides and tellurides are found in the anode mud formed in the electrolytic refining of copper and lead, this mud being the raw material for the production of selenium.

*Lead Borates.*—Lead oxide and boric trioxide melt together in all proportions, and the compounds formed are more fusible than the corresponding silicates. Advantage is taken of this fact in lead and silver assaying, by the use of borax as a flux.

*Lead Fluosilicate* ( $\text{PbSiF}_6$ ).—This is formed by the action of  $\text{H}_2\text{SiF}_6$  upon  $\text{PbO}$ , when some  $\text{SiO}_2$  is precipitated. A solution containing about 8 per cent of  $\text{PbSiF}_6$  and 11 per cent of free  $\text{H}_2\text{SiF}_6$  is used as electrolyte in the electrolytic refining of lead.

*Lead Ores.*—Lead and zinc are commonly associated in mineral deposits, sometimes intimately mixed, sometimes sufficiently segregated so that one metal predominates, but seldom free entirely from the other. The geological and geographical distribution of the two metals is, therefore, nearly identical.

All lead ores contain substances other than lead minerals. Some of these substances (e.g., gold, silver, or copper) can be recovered in the smelting process and may add much to the value of the ore. The common impurities in lead ores are silica, iron, lime, barytes, zinc, antimony, and arsenic. The first three (in minor amounts) may be beneficial or detrimental in any given ore, depending upon whether the bulk of the ore supply of the smelter carries an excess of one or the other of these elements which, in proper proportions, are required in the smelting operation. On the other hand, zinc and, to a less extent, antimony, are always detrimental and detract from the value of the ore unless separated from the lead before shipment to the smelter.

Sulphur, a constituent element of galena, is not considered a deleterious element except that carbonate ores of similar grade are more valuable, since they are cheaper to smelt. Barytes and other less common constituents of lead ores, including traces of valuable metals (bismuth, cadmium, and rare elements), are seldom present in quantities sufficient to affect the value of the ore to the miner.

The more common ore minerals of lead are:

Mineral	Formula	Percentage of lead
Galena.....	PbS	86.4
Cerussite.....	PbCO <sub>3</sub>	77.5
Anglesite.....	PbSO <sub>4</sub>	68.3
Pyromorphite.....	3Pb <sub>3</sub> P <sub>2</sub> O <sub>8</sub> ·PbCl <sub>2</sub>	76.3
Wulfenite.....	PbMoO <sub>4</sub>	56.3
Jamesonite.....	PbSb <sub>2</sub> S <sub>5</sub>	34.1

Galena is the most common and important of these minerals. The next three minerals in the list usually result from the surficial oxidation of galena, the sulphate being usually an intermediate stage in the oxidation to the carbonate. Pyromorphite and wulfenite are of minor importance. Jamesonite is considered more an ore of antimony than of lead.

Sphalerite weathers more readily than galena and zinc, and therefore is often carried below water level more rapidly and completely than lead. This fact accounts for some mines changing from predominantly lead mines to zinc mines with greater depth. Apart from the effect of such secondary enrichment, this change is often encountered in primary ores with increase in depth.

Important types of lead deposits are:

1. Deposits formed at shallow depth in sedimentary rocks without apparent connection with igneous rocks. These have evidently formed under conditions of temperature and pressure approximating those of the present surface, and occur as tabular replacements of receptive strata usually in limestones and dolomites, but sometimes in quartzites or cherts and conformable with the enclosing strata; also as irregular masses along faults, in zones of brecciation, in fissures, joints, crevices, and cavities erratically distributed in the same rocks.

In regions of slightly disturbed strata the ore shoots tend to follow pitching troughs. The ores of this type usually contain lead (galena), zinc (sphalerite), and iron (pyrite) minerals; often contain manganese and cadmium; sometimes contain cobalt and nickel, but seldom gold, silver, copper, or antimony.

The deposits of this type are of world-wide distribution and are often extensive and commercially important. Their greater purity and simplicity of treatment, particularly of the ores in their oxidized zones, caused them to be exploited first and most extensively, and to be the dominant factor in the world production of lead at one time. To this type belong, besides many others, the deposits of the Mississippi Valley and Silesia, between them producing 15 per cent of the world's production in 1913.

2. Deposits formed at shallow or intermediate depths genetically associated with igneous rocks, characterized by complex ores and comprising: (a) vein deposits apparently formed near the surface; (b) veins filled under conditions of intermediate temperature and pressure; (c) disseminated pyritic replacements of igneous rocks; (d) silver-lead replacements in limestone.

Gradations between all these types are found and many districts have related ore bodies of more than one of these types, sometimes examples of all of them.

With subtype 2a are classed certain deposits apparently formed near the surface, in genetic connection with igneous rocks and usually occurring as veins, but sometimes as stock works and pipes in volcanic rocks and adjacent sedimentaries, also as replacements in sedimentaries with associated small contact metamorphic masses near igneous contacts. The deposits are usually worked primarily for gold and silver, but small percentages of galena, tetrahedrite, and sphalerite are usually present. The gangue is largely quartz, but adularia, calcite, rhodochrosite, rhodonite, barite, fluorite, and pyrite are often present, and the presence of minerals containing arsenic, antimony, bismuth, tellurium, selenium, and rarely tungsten and molybdenum is characteristic. Successive stages of mineralization are often evident, and secondary enrichment and alteration by descending waters have disguised some deposits.

The ores of the types 2b and c are usually complex, comprising much the same minerals of zinc, lead, copper, iron, gold, and silver, and often arsenic, antimony, bismuth, and other metals. In subtype 2d, the silver-lead deposits in limestone, zinc is apparently a minor factor, but often when followed to depth, zinc replaces lead as the predominant metal. Many zinc mines are exhausted silver-lead mines.

To subtype 2a belong the deposits of the San Juan region and Lake City in Colorado, the Schemnitz deposits in Hungary, the Mapimi and Santa Eulalia deposits in Mexico, and the deposits of Insbach and Freiberg in Germany; to subtype 2b belong the deposits of Coeur d'Alene, Idaho; and to subtype 2c belong those of Bawdwin, Burma, and Ridder, Siberia. Subtype 2d comprises the deposits of Leadville, Colo., Park City, Utah, and Sierra Mojada, Mex. The importance of the ores derived from the deposits of the first three subtypes is due largely to smelting practice based on the use of lead as a collector of the precious metals.

3. Deposits in veins originating at high temperature and pressure, in, or associated genetically with, igneous rocks. The ore minerals are blende, galena, pyrite, or pyrrhotite, quartz, calcite, garnet, rhodonite, etc. To this type belong the important deposits at Broken Hill, New South Wales, Australia.

4. Igneous metamorphic deposits containing minerals characteristic of contact metamorphism. The ore minerals are galena and its oxidation products, cerussite and anglesite; blende, smithsonite, calamine, and a gangue of calcite, rhodonite, garnet, pyroxene, hornblende, magnetite, and tremolite. Among the deposits of this type are those of Magdalena, N. M., and the Horn Silver mine, Utah, occurring on or near contacts of limestone with igneous rocks.

**Recovery of Lead from Ores.**—Metallic lead has been recovered commercially from its ores almost exclusively by smelting in carbon-heated furnaces—either blast or ore hearth—until very recent years. Electric furnaces have been used for complex-ore reduction, but have not become of practical utility, and it would seem that no great promise of development exists in this direction as far as lead is concerned, due to the high volatility of lead compounds at the operating temperatures obtained in electric-furnace work.

Various processes intended to make available ores of low grade, or complex ores of lead and zinc, have received considerable experimental attention in the period 1918–1925, and during these later years a number of commercial plants have gone into operation along hydrometallurgical lines which have been the subject of investigation for many years past. Among these, the brine-leaching methods and the chloride-volatilization processes are by far the most important, the former in the field of complex zinc-lead sulphide (and oxide) ores, the latter more particularly in the field of oxidized and semioxidized (and sulphide) ores of copper, lead, zinc, and silver.

The hydrometallurgical treatment of lead ore has reached a point where it has begun economic competition with concentration and blast-furnace smelting on many

sulphido ores. The net recovery with mill and smelter approximates 85 per cent; leaching with or without roasting will recover 95 per cent. The mills and smelters already in existence will doubtless continue to operate, but the economic warrant for the erection of smelters will be more carefully considered in the future. In general, lead can be produced, at present, more cheaply by smelting than by leaching, if the material to be treated contains over 12 per cent of lead.

**Brine-leaching Methods.**—These involve the roasting (sulphating or chloridizing) of the sulphides, solution of the stable lead-silver compounds in acid brines, and the final recovery of the lead by electrolysis or, less frequently, by precipitation on scrap and sponge irons. Although two plants in Utah are in operation, using the latter method of precipitation, the profitable extraction and recovery of lead by this means has not yet been entirely worked out. The free sulphuric acid in the lixiviant limits the dissolution of the lead; when an average of 8 lb. of metallic lead per ton of mill solution has been precipitated, the same lixiviant will dissolve more lead. Commercial brine-leaching plants have been, or are, in operation at several points: Kellogg, Idaho; Tintic, Utah (two); Great Falls, Mont.; Kennett, Cal.; Trail, B. C.; Australia; and England.

An important plant, using the Tainton process of brine leaching, went into operation in 1923 in Idaho, the result of extensive experimenting for several years by the Bunker Hill & Sullivan company. In general, the process adopted involves the roasting of galena to sulphate in an electrically heated rotary cylinder, at 500°C., the removal of soluble sulphates of manganese, magnesium, and other metals by water wash, the solution of lead sulphate in a brine that is saturated with salt and contains dissolved chlorine from the electrolytic cells; and the precipitation, by electrolysis—with high current density and high acid strength—of lead and silver in a cell with rotating sheet-iron cathodes and graphite anodes. The sponge lead recovered is thrown off the cathode by centrifugal force and floats out of the cell with the brine, or settles at the bottom of the cell, and is pressed into cakes for melting. A 95 per cent extraction of the silver and a 95 to 98 per cent extraction of the lead is possible. The process is expected to be applicable to electrolytic zinc tailings, and well as for the huge accumulation of tailing from the lead concentrator on which it is operating at the start.

In this Idaho application of brine leaching, the preliminary roasting of the galena is a simple low-temperature sulphating roast (400 to 500°C.), without chloridizing, and the solution of the lead is made possible by the presence of dissolved chlorine in the brine. Ordinarily, and in the majority of other brine-leaching plants, a chloridizing roast is utilized to convert the lead sulphide into soluble chloride form.

Electrolytic-zinc-plant tailings, lead sulphate flue dust, lead sulphate sludges from sulphuric acid chambers, oxidized ores of lead containing carbonate or sulphate, concentrating-mill tailing containing lead and silver sulphides, and complex zinc-lead-iron sulphide ores comprise the products to which the brines have been adapted.

Brines, containing dilute hydrochloric acid, and also sulphuric acid, are applied in some cases directly to the raw sulphide ores, attacking the galena and leaving the zinc sulphide largely untouched.

The Snyder-Christensen process, in operation at Bauer, Utah, by the Combined Metals Reduction Co. is based on this principle. An auxiliary to the main plant is one for the manufacture of hydrochloric acid according to standard practice. From a technical standpoint the process can extract lead from almost any mineral product containing the metal; its practical application is confined to

materials that for any reason cannot be treated advantageously by concentration and smelting alone.

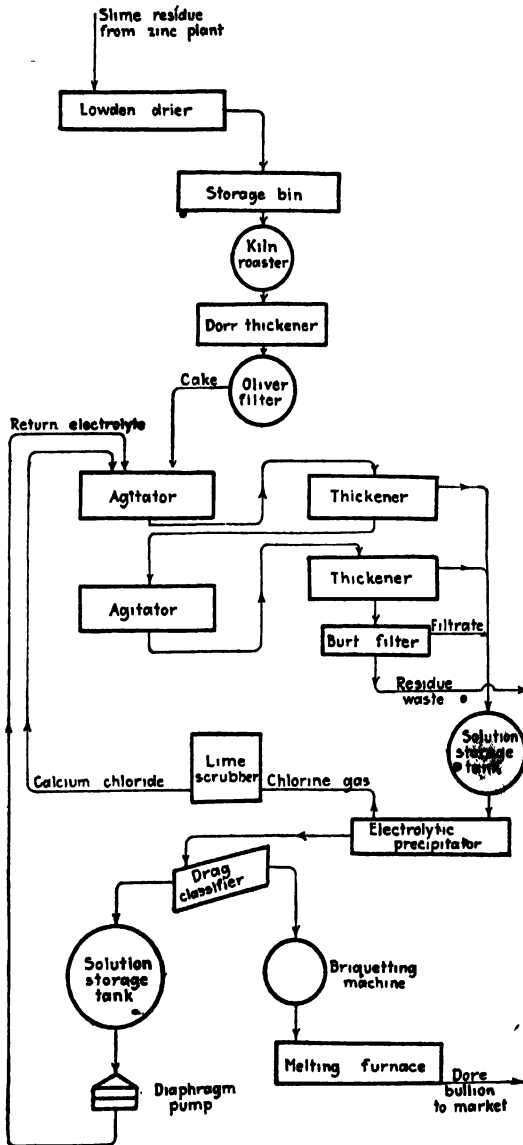


FIG. A.—Flow sheet, Tainton process.

The features of the treatment are the leaching by agitation of unroasted ore in a hot brine solution containing a small quantity of hydrochloric acid; filtration



and washing with hot, weak solution and water; precipitation of the silver by means of lead in some form; precipitation of the lead by cooling the pregnant solution; and reduction of the lead by melting with a mixture of lime and coal dust. The solutions are circulated through "spray heaters" for reuse. The lead precipitation is based on the simple fact that a hot liquor at 90°C. will hold 8 to 10 per cent lead, whereas when cooled to 30°C. only 1 per cent will remain in solution. The most important difference between this process and that used by the Tintic Standard Mining Co. at Harold, Utah, is that a chloridizing roast is eliminated. When ground very fine, galena will dissolve in a hot, saturated, and acidulated brine. The precipitation is likewise different, as in the Tintic Standard plant detinned iron scrap is used as a precipitant.

Brines carrying ferric chloride are adapted to removing silver, copper, and lead from complex sulphide ores, and have been in use in Canada, England, and Utah. These ferric brines are more widely used for leaching prepared ore than for attacking raw ore. Whereas lead can be dissolved in a neutral brine, the silver is so easily precipitated from the solution on such substances as zinc sulphide that almost invariably the brine must also contain small amounts of acid or of ferric chloride or cupric chloride, all of which tend to redissolve any precipitated silver sulphide.

A practical method for removing lead and silver from zinc sulphide has been developed in Australia, consisting of mixing the ore with sufficient zinc chloride to supply 33 per cent excess chlorine over that necessary for combining with the lead, silver, arsenic, antimony, and tin in the ore, and heating to 400 to 500°, out of contact with air. Chlorides of arsenic, antimony, and tin are volatilized, and chlorides of silver and lead remain in the anhydrous mass. These are leached in brine containing hydrochloric acid and ferric chloride.

**Chloride-volatilization Processes.**—These involve the chloridizing roast of the ore and the precipitation of the fume so produced by Cottrell electrostatic apparatus. There have been four commercial, or semicommercial, chloride-volatilizing plants, all at present shut down, work having been discontinued in 1920 and 1921 owing to low metal prices. The Western Metallurgical Co. started operations in Arizona in 1924. Except for the limitation of fume recovery to electrical apparatus, chloride-volatilizing methods are, in general, adapted to a wider range of ore and are less sensitive to trouble than the brine-leaching processes. Metallic chloride vapors condense as colloidal particles of fume, each surrounded by adsorbed films of air or gas, which prevent collection by any other means than electrical precipitation. These particles pass untouched through water or any form of scrubbing device; but the electrical stresses of the Cottrell field break up the gas envelopes. Bag houses of textile filters will make a high recovery, but the corrosive action of fumes and gases rapidly destroys the fabrics.

The field of chlorine in lead metallurgy is important, and is discussed elsewhere in the present volume.

**Miscellaneous Processes.**—Direct sulphuric acid treatment of mixed sulphide ore is receiving attention in England and Burma, but no wide success has been attained. In one Elmore process strong acid (95 per cent  $H_2SO_4$ ) at about 100°C. converts galena to lead sulphate, which is later removed by brine, and zinc sulphide is largely unaffected, while in the Christensen method a treatment of the complex zinc-lead ores has been developed with acids weaker than 80 per cent, which produces almost the opposite result.

## LEAD

An old process restored to active consideration in recent operations, the Canelin dry process, is reported in late use at Newcastle, England, in the treatment of Burma zinc-lead middlings, and sulphides. This method consists in feeding the pulverized ore—60 mesh—into a molten bath ( $550^{\circ}\text{C}.$ ) of  $\text{ZnCl}_2$  and  $\text{NaCl}$ . Zinc replaces lead and silver, which are dissolved as chlorides,  $\text{ZnS}$  being precipitated. The lead and silver are then precipitated as metals by granulated spelter, added in the amount of 35 per cent of their weight, the dissolved spelter forming  $\text{ZnCl}_2$ . The silver-bearing lead is siphoned out of the cast-iron kettle in which the reaction has taken place, the residue granulated, the salts leached with water, and the zinc-bearing gangue freed from lead shot by tabling, leaving a zinc ore free from lead. Theoretically, there is no loss of reagent, and this old process is at first sight very attractive. It has had a most serious and costly revival by one of the major lead producers recently, and although its users feel that there may be conditions under which it might be valuable, it has been again abandoned. The chief cost is not in the manipulation, but there proves to be a heavy expense in cost and losses in the circulating load of metallic zinc. Recoveries are excellent, a 30 per cent lead-bearing zinc concentrate being reduced in lead to 1 per cent, and the silver from 35 oz. to 1 oz.

It is claimed that the hydrometallurgical method, not using brines—the sulphate, or Coolbaugh process—yields good results in the treatment of complex lead-zinc-copper ores which will not yield to mechanical concentration as a means of separating zinc from lead or copper. The ore is roasted ( $550$  to  $700^{\circ}\text{C}.$ ), to produce the maximum amount of sulphates. Towards this end, the  $\text{SO}_2$  is used over again, converted by ferric oxide and other catalyzing agents into the trioxide, and a thorough sulphating of the  $\text{ZnO}$  accomplished. The calcines are leached with water to separate the soluble zinc and copper sulphates from the balance of the mineral. Copper is precipitated from solution by zinc, and the zinc sulphate is either evaporated to crystallization, and used in the lithopone industry, electrolyzed for metal, or the zinc is precipitated in neutral solution. The residue containing lead, copper, and other metals, if any, is sintered and smelted as a zinc-free product. Processes of this character belong perhaps more directly to the metallurgy of zinc than to that of lead.

A process on which considerable experimental work has been done in Colorado is the so-called Gordon "gas-house-liquor" process. It deserves mention, perhaps, because it seems theoretically sound. It is suitable mainly for treating typical zinc-iron-lead middlings. They should be low in iron to minimize the formation of insoluble ferrites, and low in lead. Briefly, the process consists of roasting; leaching zinc and copper with an impure ammoniacal menstruum; precipitation of copper with zinc, and of zinc as a carbonate in standard ammonia stills; and calcination of the carbonate to impure zinc oxide. The feature of the process is the use of by-product gas-house liquor as a cheap source of ammonia.

The art of smelting lead ores is based on these three principles: (1) the reduction of lead oxide by carbon or carbon monoxide; (2) the reaction between lead sulphide and lead sulphate or oxide, resulting in a double decomposition with the formation of lead and sulphur dioxide; and (3) the decomposition of lead sulphide by metallic iron. All of these reactions are endothermic, i.e., they require heat supplied extraneously.

The first principle is the basis of what is known as the roast-reduction (or blast-furnace) method of smelting, in which lead oxide, lead silicate, or other oxidized compound must first be prepared from sulphide ore by a roasting operation.

The second is what is known as the roast-reaction or air-reduction method—the basis of reverberatory and ore hearth smelting. The third is the basis of the precipitation method.

All of these methods are employed practically in the United States at the present time, either alone or in combination, the latter being more commonly the case; also, the principles are not practically so sharp as theoretically stated, the reactions fundamental to one process invariably playing a certain part in the other processes.

If a lead ore were absolutely pure, there would be no other consideration in the smelting processes than those reactions which relate to lead and its chemical combinations; but, practically, lead ores are never pure, the valuable minerals being mixed with a certain proportion of foreign matter, which must be separated by making a slag of it. In the roast-reaction method of smelting, it is true, no slag, properly speaking, need be made, the reduced lead being liquated out from the worthless impurities, but the latter will still retain a high percentage of lead, and, in order to effect a high degree of extraction from the ore, it must be subjected to a further smelting process in which a true slag is made. In making a slag, the object is to combine the impurities into a fusible silicate, which, when molten, will be of comparatively low specific gravity, so that the heavier lead will settle to the bottom of the crucible of the furnace, whence it may be drawn off separately, while the lighter slag will float on top. Besides the slag and metal, there is formed another substance, matte, which is lighter than the metal but heavier than slag. Matte is an artificial sulphide, consisting in lead smelting usually of the sulphides of iron, lead, and copper (if copper be present in the ore), and owes its origin to the incomplete elimination of sulphur from the ore. Similarly, speiss is an artificial arsenide of iron.

The difference between lead smelting in principle and in practice is chiefly due to the incompleteness with which the basic reactions are carried out, and the qualifying effect of the impurities that are commonly met with in ores. Thus certain metallic impurities are reduced with the lead, contaminating it and necessitating a subsequent refining process. Other impurities affect the composition of suitable slags. Others affect the running of the furnace in various ways.

If the ores are free from silver, the lead resulting from the smelting process is usually of market grade after it has undergone a slight purification by liquating and poling. In a few instances, "silver-free" (Mississippi Valley), lead undergoes treatment by the Parkes desilverizing process, as the amount of impurity present is considerably reduced, and the higher price received for the better grade of lead and the small amount of silver recovered make the operation profitable. If the ore is argentiferous, as is the case with practically all districts outside the Mississippi Valley, the silver passes, for the most part, into the lead bullion, and the latter is then desilverized by either the Parkes or the Pattinson process.

The smelting of lead ores is carried on in three types of furnaces: the reverberatory, the ore-hearth, and the blast furnace. Of these, the first has become almost obsolete; the ore-hearth in recent years has become of considerable importance with a limited class of ores; the blast furnace remains the leading method, as it can treat economically all kinds of ores.

**The most primitive form of lead smelting** in the United States was practiced with the log and ash furnaces in Missouri prior to 1850. They employed the roast-reaction system of smelting and were applicable only to non-argentiferous galenas, of very high grade in lead. They were for the most part displaced about 1840 by the Scotch-hearth furnace. Later, reverberatory furnaces of the Flintshire type came into use, but never extensively, nor with such success as to develop a permanent metallurgical practice. The Scotch hearth, however, has survived, and in its modern development is the basis of a highly efficient process in the treatment of certain classes of ore, especially high-grade non-argentiferous galena.

Neither the Scotch hearth nor the reverberatory furnace is well adapted to the treatment of argentiferous ore, or to the treatment of ore containing less than 60 per cent of lead, while the smelting of carbonate ores alone in these ways is not feasible. For these reasons by far the major part of the world's lead is produced by smelting in the blast furnace.

**In smelting any kind of lead ore** in any way, the sulphur must be burned off, partly at least, and the impurities must be combined in a slag, fusible at approximately 1100 to 1200°C., and of specific gravity not to exceed 3.6, or but little more. The slag must be of a composition which will form at the right point in the smelting process, will be thoroughly liquid, in order to insure a satisfactory separation from the matte, and will require the minimum consumption of fuel, the chief part of which in blast-furnace smelting is always consumed in effecting the formation of the slag.

**The sulphur is eliminated in various ways**, which may be enumerated as follows:

1. *Roasting*.—Lead ores, being usually low in sulphur, are not self-burning in the ordinary roasting furnace. As the decomposition of lead sulphate is effected only by reaction with silica, forming lead silicate, the necessary temperature must be chiefly supplied by the combustion of carbonaceous fuel. The roasting of lead ore may be done in three ways, *viz.*:

a. Ordinary roasting, in which the ore is simply desulphurized, at the same time being more or less sintered. Often the ore is partially fused, so that upon withdrawal from the furnace it crusts or may be pounded into cakes.

b. Slag roasting, in which the ore is completely fused.

c. Blast roasting, in which the sulphides are self-burned and sintered under air blast, either pressure or suction.

The object of roasting is to reduce the sulphur as low as possible, without entailing undue losses in other directions. The sulphur is more completely eliminated by sinter roasting than by ordinary roasting, and more completely by slag roasting than by sinter roasting, but at the same time the loss of lead by volatilization is heavily increased, and in slag roasting is so high that the process has been abandoned in the United States, save in one or two instances. Ordinary roasting, by which the sulphur is reduced to about 4 per cent, had become the generally adopted method until recently displaced by the "blast-roasting" process.

The subject of roasting, in general, finds detailed treatment in another section of this volume.

2. *Roast Reaction*.—Lead sulphide burned partially to sulphate reacts with undecomposed sulphide, setting free metallic lead and sulphur dioxide. This process is effected in the reverberatory smelting furnace (Flintshire, Tarnowitz, etc.) wherein the charge is first partially roasted and the reaction is then effected under increase of temperature; also in the Scotch hearth, wherein the roasting and reacting go on contemporaneously. In the modern blast furnace, which has lines and is operated under conditions promoting oxidation, roasting and reacting play an important part.

3. *Precipitation*.—In this method the ore is charged raw into the blast furnace and the lead sulphide is decomposed by iron, precipitating metallic lead, while the sulphur combines with the iron, forming a matte, from which the sulphur is subsequently eliminated by roasting. The quantity of matte to be roasted is apt to be as much as the quantity of ore smelted, but the loss of lead is less than if the ore were roasted originally. There are other drawbacks, however, and this method, which has never

and ameliorated labor conditions, an important item in view of the severity of the latter, especially in hot weather.

**The Blast Furnace.**—The lead blast furnace has become in recent years practically standardized at modern plants, in probably its maximum dimensions. Materials going into, and products coming out of, the furnace are handled in

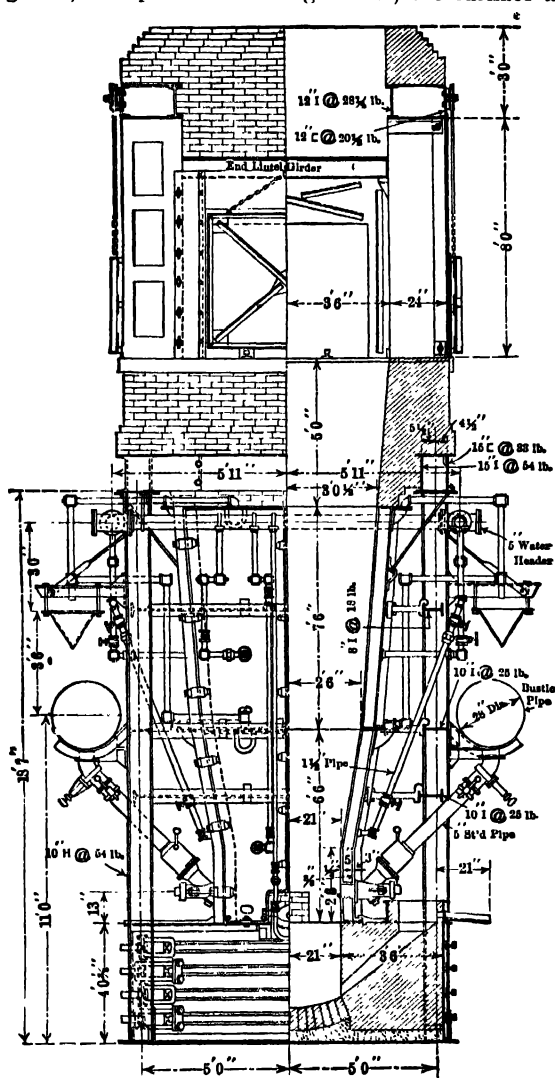


FIG. 1.—Blast furnace, Northport Smelting & Refining Co.

almost as many different ways as there are plants in the industry. In this respect also, there is a tendency toward standardization, as hand labor becomes gradually replaced by machinery. Lead blast furnaces have certain common features, in general—rectangular horizontal section, tapering sides with boshes,

straight ends, a water-jacketed smelting zone, internal crucible, and the Arents siphon tap for lead. The circular water-jacketed furnace is used only to smelt at intervals small quantities of intermediary products of a refinery, or for ore smelting in remote localities. The brick shaft common with most ore furnaces has in some of the recently built plants been replaced in its lower portions by steel water jackets.

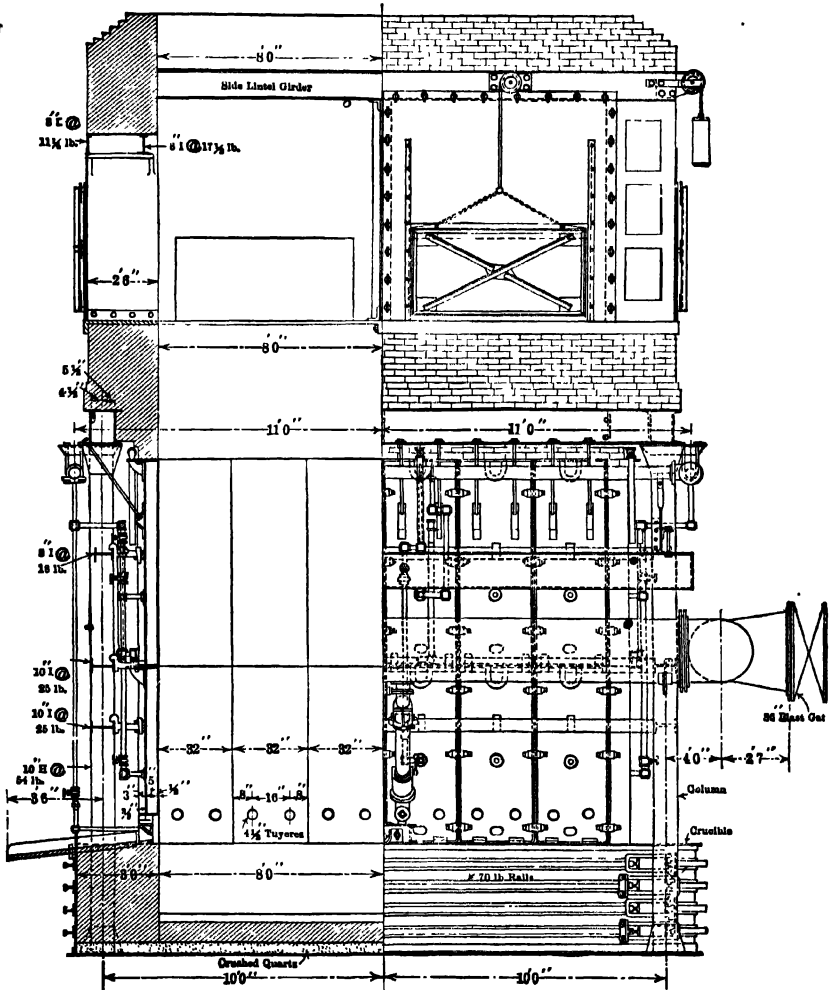
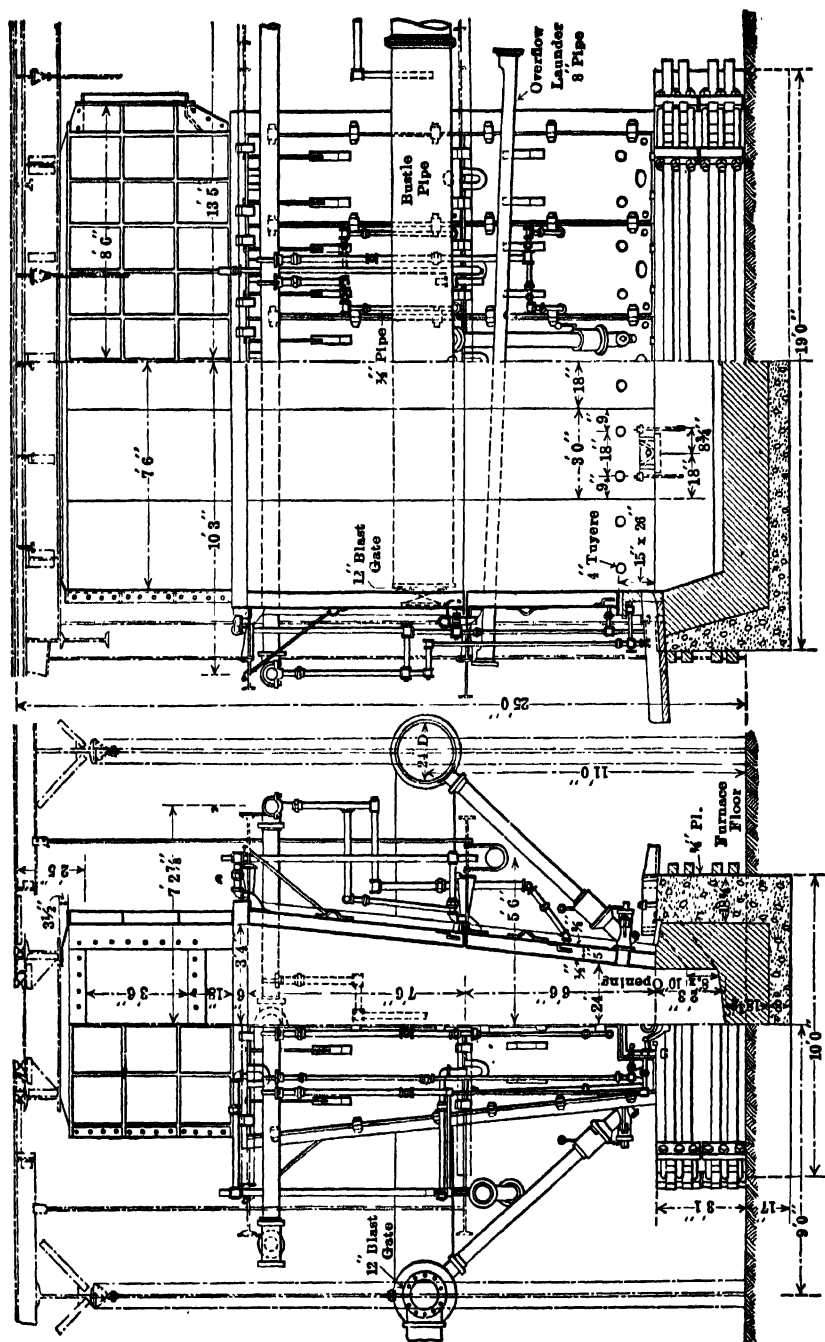


FIG. 2.—Longitudinal section, Northport furnace.

With the increase in size of furnaces and of smelting plants the transportation of ore, flux, and fuel by teams and wheelbarrows, became impossible, and reliance on hand labor for manipulation less and less efficient, and these early methods have



Figs. 3-4.—Bunker Hill & Sullivan Mining & Smelting Co.'s blast furnace.

largely given way to mechanical traction and handling. The accessory apparatus for removing slag from the early small-size furnaces treating mainly oxide ores consisted simply of pots pushed by laborers. As oxide ores were replaced by sulphides, matte handling became a problem in connection with slag handling, solved by extra settling pots which have now given way to large forehearth. As tonnages continued to increase, and speiss, dross, furnace accretions, and refractory slags came into the picture in the various smelting centers, compressed air, water, steam, and electric power were brought into play, and mechanical traction, slag granulation, and mechanical furnace manipulation, in general, are found throughout the industry.

The waste gases in early lead smelting escaped to the atmosphere, carrying damage to crops and men in the immediate vicinities of the plant; in later periods settling chambers for catching dust from the smoke stream were provided, and these have been supplemented and replaced now by bag houses for filtering, and electrical condensing apparatus for precipitating, the dust. The primitive blowing engines adequate for blast requirements at first, have been superseded by rotary pressure and centrifugal blowers.

The standard form of lead blast furnaces is illustrated in the equipment erected in recent years at the Northport,<sup>1</sup> Wash., and Kellogg, Idaho, plants.

The dimensions, and principal facts of operation (1924) of some of the leading furnace plants of the United States and Canada, and Australia, are assembled in the table on pages 876 to 879.

In considering the lead blast furnace the following points may be mentioned. The weight of a modern furnace with brick shaft is something over 100 tons. The shaft, the heaviest part, is carried on four cast-iron or steel columns, one at each corner, resting on a concrete foundation extending about 3 ft. beyond the bedplate and supporting columns.

The height of the shaft, i.e., the smelting column, extending from the tuyères to the feed floor or to the bottom of the down-take flue for gases, varies at different plants, the tendency being to increase as time goes on. Twenty-five years ago the distance from tuyères to feed floor was from 10 to 12 ft.; this later became 14, then 16 (a common dimension in recent years), and has been carried as high as 24 to 28 ft., with notable success in Australia on charges high in zinc (Sulphide Corporation). The increase in height has followed the greater volume and pressure of blast required by the gradual enlargement of capacity and smelting power of furnaces operating on siliceous and limey slags instead of those running high in iron, and on charges carrying heavy zinc burden. Blast pressures, formerly 8 to 10 oz. per square inch, range at present from 30 to 40 oz., and in the case of the Sulphide Corporation, New South Wales, were 70 oz. at the time of suspending operations at that plant in 1922.

The horizontal section of the furnace is rectangular, the width being most commonly 48 in., ranging from 36 to 60. The distance between tuyères is limited because of the excessive blast pressure which would be required to penetrate to the center of larger furnaces which would cause excessive volatilization of lead. When furnace charges consisted largely of fine material, the usual distance was 42 in.; with blast-roasted ore and a coarser charge this dimension increased to 54 and to 60 in., although 44 and 48 in. are the more common figures.

Enlargement of the lead blast furnace has taken the direction, inevitably, of increased length rather than breadth, doubling from the old 60 in. to 120 in., and later increasing to 160, 180, and 192 in. The limit to which the length of a lead furnace can be efficiently increased is an open question. A normal crew can serve a furnace, say, 152 in. long; if this be increased, extra men are necessary, and the additional tonnage obtained is not equivalent to the added cost of labor. Some furnace men hold

<sup>1</sup> These furnaces have been transferred bodily to the East Helena plant of the American Smelting & Refining Co. (1922) following the shutting down of the Northport plant.



## BLAST FURNACES

	National Lead Co. Collinsville, Ill	Consol. M. & S. Co., Trail, B. C	U. S. S. R. & M Co., Midvale, Utah	American Smelting & Refining Co.		
				Selby, Cal.	Arkansas Valley, Colo.	Murray, Utah
Horizontal section at throat (feed-floor), inches . . . . .	156 × 54	84 × 180	95 × 160	60 × 156	84 × 180	93 × 176
Area at throat, square feet . . . . .	58.5	105	105.55	63	103	113.66
Horizontal section at tuyères, inches . . . . .	36 × 126	50 × 180	48 × 160	36 × 144	44 × 162	48 × 176
Area at tuyères, square feet . . . . .	31.5	62.5	53.33	36	49.5	58.96
Ratio throat to hearth area . . . . .	1.8	17 ft 3 in	24 ft 8 in	1.80	7.12	38.94
Height, tuyères to throat (feed-floor) . . . . .	20 ft 9 in	15 ft 3 in	16 ft 0 in	27 ft 6 in	19 ft 6 in.	24 ft 6 in.
Height, tuyères to top of crucible, inches . . . . .	13 ft 9 in	15 ft 3 in	16 ft 0 in	21 ft 6 in	19 ft 6 in	16 ft.
Height, tuyères to top of steel . . . . .	11 ft 6 in	12	13	12	16	15
Water jackets, cast-iron or steel . . . . .	Steel	Steel	Steel	Cast iron	Steel	Steel
Water jackets, number on one side and end . . . . .	4S 2E	6S 2E	5S 1E	8S 3E	4S 1E	6S 2E
Water jackets, height . . . . .	4 ft 6 in	14 ft (2)	6 ft 0 in	4 ft 6 in	5 ft 0 in.	5 ft 11 in
Boosh, height . . . . .	3 ft 2 in	4 ft 0 in	4 ft 1 in.	3 ft 1½ in.	3 ft 2 in.	4 ft 2¾ in.
Tuyères, number on a side . . . . .	8	2 25	4 41	3 87	2 21	2 365
Tuyères, diameter, inches . . . . .	8	12	10	8	12	10
Tuyère-ratio . . . . .	6.4	4	4	3½	4	4¾
Crucible, section at top, inches . . . . .	116 × 36	2 41	4 71	3 41	6 09	4 84
Crucible, section at bottom, inches . . . . .	116 × 36	180 × 50	160 × 18	144 × 36	162 × 44	160 × 44
Crucible, depth, inches . . . . .	116 × 36	168 × 50	150 × 30	144 × 36	148 × 24	160 × 44
Crucible, depth, feet . . . . .	28.000	85.000	32.5	27	15.4	30
Lead well, area of channel . . . . .	8 5 × 8 5 in	80 in from front	6 × 6 in	40 000	40 000	80 000
Lead well, height of basin, inches . . . . .	10 × 10	8 × 10 in	12 × 12	Center	31 in from front	40 in from front
Lead well, height of top of basin above top crucible, inches . . . . .	6	12 × 14	10	9 × 9	12½ × 13½ in	9 × 9
Forehearth, inside length × width × depth, inches . . . . .	63 × 30 × 30	60 diam. 30 deep, circular	108 × 54 × 12	72 × 96 × 27½	82 × 41 × 38	97½ × 43½ × 34
Forehearth, capacity, cubic feet . . . . .	32.8	30	40	68	73	83.5
Waste slag pots, capacity each, cubic feet . . . . .	21	30	8	25	20	25
Charge (ore and flux), weight, pounds . . . . .	8,000	(Granulate) 6,500	8,700	10,000	6,000	8,000
Charge, in tons, weight, per cent . . . . .	0	300	30-65	76	55	52.4
Charge, in 24 hr, weight, per cent . . . . .	248	350	160-300	200	160	263
Charge, tons per square foot hearth area, 24 hr . . . . .	7.92	5.6	4.52	5.55	3.2	4.48
Pb, per cent of charge . . . . .	39.8	35-40	11-18	20-30	0.8	12.8
Cu, per cent of charge . . . . .	1.2	Small	0.7-1.0	1.0	0.8	1.02
S, per cent of charge . . . . .	3.0	1.0	2.5-3.8	3.0	4.0	3.5
Coke, per cent of charge . . . . .	10.0	11.5	12.0	12.5	12.0	11.85
Coke, per cent of carbon . . . . .	82.0	82.5	85.0	82.0	76.0	81.4
Coke, per cent of ash . . . . .	14.0	13.0	11.0	13.0	21.5	14.1

Blast, cubic feet per minute.	8,000	5,200	6,000	5,000-6,000
Blast, ounce pressure.	26-32	36-42	40	35
Cooling water for jackets, gallons per hour.	9,000	Variable	Variable	Variable
Men in 8-hr. shift, regular crew	7	6	5	8
Lead bullion, ounces Ag, Au, per ton	10.0	50.0	245	160, 3.60
Speiss, per cent charge.	None	Small	0.5	
Matte, per cent charge	8.3	None	10.0	9
Matte, Pb, per cent.	17.0		10-18	12
Matte, Cu, per cent	7.0		6-12	4-8
Matte, Ag, ounces per ton	5.2		30-50	20-40
Slag, SiO <sub>2</sub> , per cent	29.1	18.0	34.0	25-27
Slag, Fe(Mn)O, per cent	33.7	42.0	28.0	40-36
Slag, Ca(Mg)O, per cent	16.5	10.5	22.0	17-19
Slag, Al <sub>2</sub> O <sub>3</sub> , per cent	4.0	5.5	3.0	3.5
Slag, ZnO, per cent	11.4	19.0	5-9	6.0
Slag, Pb, per cent.	1.5	1.5	0.6-1.2	0.9
Slag, Ag, ounces per ton	0.2	0.15	0.5-0.7	1.0
Slag, Cu, per cent				0.5
Slag, specific gravity				3.14

<sup>1</sup> Tuyère-ratio = square inch tuyère area: square feet hearth.

<sup>2</sup> Charge almost exclusively gray slag from ore-bearths.

<sup>3</sup> Smelting discontinued, 1922.

## BLAST FURNACES.—(Continued)

	American Smelting & Refining Co.				St. Joseph Lead Co., Herculanum, Mo.	Sulphide Corporation, Rooderoo, N. S. W.	Bunker Hill M. & C. Co., Kellogg, Idaho
	East Helena, Mont.		Federal, Ill				
	Fees 1, 2, 3	Fee 4					
Horizontal section at throat (feed-floor), inches	84 × 192	90 × 170	78 × 144	84 × 192	123 × 201	80 × 180	
Area at throat, square feet	112	106	78	112	171.67	100	
Horizontal section at tuyères, inches	42 × 192	48 × 136	42 × 144	43 × 192	60 × 138	48 × 180	
Area at tuyères, square feet	56	45	42	57	57.5	60	
Ratio throat to hearth area	2	2 4	1.86	1.97	2.98	1.66	
Height, tuyères to throat (feed-floor)	24 ft. 1 in.	24 ft. 1 in.	21 ft. 0 in.	20 ft. 0 in.	29 ft. 8 in.	20 ft. 9 in.	
Height, active or working	15 ft.	Thimble	14 ft. 6 in.	11 ft. 0 in.	24-28 ft.	14 ft. 10 in.	
Height, tuyères to top of crucible, inches	10	12	Steel	Steel	16	14	
Water jacketa, cast-iron or steel	128 4E	Cast iron	58 1E	48 1E	88 3E	58 4E	
Water jacketa, number on one side and end	14 ft (6 ft 6 in.)	4 ft 6 in.	5 ft. 9 in.	6 ft. 0 in.	6 ft. 6 in.	14 ft. 6 in.	
Water jacketa, height	+ 7 ft. 6 in.)	3 ft. 0 in.	4 ft. 8 in.	3 ft. 11 in.	4 ft. 4 in.	14 ft. 0 in.	
Bosh, height	0 75	0.64	2	3	4.2	1.25	
Bosh, inches per foot, height	12	8	8	12	7	10	
Tuyères, number on a side	4 1/2	5	4	4 3/4	3	4	
Tuyères, diameter, inches	3.50	4.40	4.79	6.35	1.72	4.19	
Tuyère-ratio	192 × 42	136 × 48	42 × 144	42 × 188	54 × 132	45 × 180	
Crucible, section at top, inches	192 × 42	120 × 48	24 × 144	42 × 168	54 × 132	45 × 168	
Crucible, section at bottom, inches	36	33	24	28 1/2	20	27	
Crucible, depth, inches	90,000	80,000	40,000	50,000	38,500	80,000	
Crucible, holds pounds lead	At second jacket	At second jacket	48 in. from front	At fifth tuyère	Center side	54 in. from front	
Lead well, position	24 sq. in.	24 sq. in.	4 × 4 in	8 × 8 in.	4 × 4 in.	8 × 10 in.	
Lead well, area of channel	9	9	4	6	10	6	
Lead well, area of basin, inches	102 × 42 × 33	102 × 42 × 33		98 × 51 × 35		Two circular, 6 ft. 2 1/4 in. top, 3 ft. 8 in. bottom, and 5 ft. depth, and 5 ft. top, 3 ft. 6 in. bottom, 2 ft. 3 in. depth.	
Lead well, height of top of basin above top of crucible, inches	9	9	4	6	10	6	
Forehearth, inside length × width × depth, inches.	102 × 42 × 33	102 × 42 × 33					
Forehearth capacity, cubic feet	83	83		100	1-ton pot	50	
Waste slag pots capacity each, cubic feet	28	28		23	3	130	
Charge (ore and flux), weight, pounds	9,000	9,000	5,600	12,000	2,250	\$,800 to 7,600	
Charge, blast-roasted, per cent	75	75	70	75 to 85	75	60 to 76	
Charge in 24 hr., short tons	260	220	214	374	936	325	

Charge, tons per square foot hearth area, 24 hr . . . . .	4 7	4 8	5 1	6 56	5 81	5 4
Pb, per cent of charge	24-28	24-28	35-45	45-50	33	25-35
Cu, per cent of charge	Very small	Very small	3 8	0 4	None	None
S, per cent of charge	3 0	3 small	3 8	3 4	2 0	Small
Coke, per cent of charge	12 4	12 4	12 9	8 4	12 0	9.5 to 14
Coke, per cent of carbon	82 0	82 0	79 0	82 0	83 0	78 to 82
Coke, per cent of ash	15 0	15 0	14 0	7 0	12 0	12 to 16
Blast, cubic feet per minute	7,000	5,000	6,900	7,000	7,500	6,000 to 7,000
Blast, ounces pressure	32-36	32-36	26	22-36	70	26 to 32
Leading water for jackets, gallons per hour	6,000	5 00		15,000	12,000	
Leading water for regains, gallons per hour	3	3				
Lead bullion, ounces Ag, Au, per ton	80	80	Ag, 1 7 Au, 0	Ag, 3 8 Au, 0	80	Ag, 60 to 100 Au, 0 25
Speiss, per cent charge	None	None		None	None	None
Matte, per cent charge	None	None	5 7	2 5	None	None
Matte, Pb, per cent	None	None	22 0	12 0	None	None
Matte, Cu, per cent	None	None	12 0	4 0	None	Small
Matte, Ag, ounces per ton	None	None	2 0	0 75	None	None
Slag, SiO <sub>2</sub> , per cent	21-25	21-25	20-30	2 4	38	20-33
Slag, Fe(Mn)O, per cent	45-39	45-39	30-35	40	38	35-28
Slag, Ca(Mg)O, per cent	13-15	13-15	14-16	14	17	16-21
Slag, Al <sub>2</sub> O <sub>3</sub> , per cent	3 6	3 6	7 5	3 8	5	4-6
Slag, ZnO, per cent	15 0	15 0	8 5	12 0	12	5 to 10
Slag, Pb, per cent	1 0	1 0	1 0	1 1	0 6	1 0
Slag, Ag, ounces per ton	0 35	0 30		Trace		0.15 to 0.40
Slag, Cu, per cent						
Slag, specific gravity			3 65	3 8		3 4

<sup>1</sup> Tuyère-ratio = square inch tuyère area ÷ square feet hearth area

<sup>2</sup> Charge almost exclusively gray slag from ore-hearths.

<sup>3</sup> Smelting discontinued, 1922.

that 152 in. is the maximum economic length with a single slag tap; others say 192 in. No great success has been attained in imitating, on the lead furnace, the great increase in length that has been such a notable development of the copper blast furnace, with double complement of slag taps and lead wells, as lead smelting is a more delicate matter than copper smelting. When a lead-smelting furnace becomes unsatisfactory it is usually cheaper to blow down the furnace, bar out, and start fresh instead of attempting to nurse it back to normal work. With a copper furnace this is done more readily than with a lead furnace, and with less loss of metal. The larger and higher lead furnaces have shown, within limits, a greater smelting power than was expected from the increased hearth area, and the increased tonnage has been accompanied by a lower fuel consumption.

The vertical section of a lead blast furnace is marked by side boshes, and a contracted tuyère section. This contraction secures a more rapid combustion and concentrated, intensified heat, resulting in a quicker fusion and more complete decomposition of sulphide of lead. Then when, higher up in the shaft, the width is suddenly increased by the boshes, the gases formed at the tuyères are checked in their upward velocity and more evenly diffused through the descending ore column, giving up their heat to the charge, and preparing it for subsequent fusion. In addition, the spread of the gases decreases the amounts of flue dust.

The ends of the furnace are usually without bosh, although some of the earlier plants have end bosh as well as side. Experience generally indicates that the end bosh tends to bring about wall accretions.

Extending from the bottom of the brick shaft to the top of the crucible are the water jackets—water cooled iron or steel shells that enclose the smelting zone to protect the furnace from corrosion by the slag. A substantial amount of furnace heat, perhaps 10 per cent, is carried away by the cooling water of the jackets, but they are essential to efficient operation.

The tuyères—circular orifices through the jackets, usually placed about 13 in. above the bottom, 4 to  $4\frac{1}{2}$  in. in diameter—permit the entrance of the blast to the smelting zone. They are placed along the sides and back of the furnace, and with centers 16 to 20 in. apart. The modern furnace takes from 5,000 to 8,000 cu. ft. of air per minute.

✓ The hearth, or crucible, enclosed in brick, concrete, and iron work, extends from the foundation to the bottom of the jackets. The lines of the crucible are usually a continuation of those of the shaft, and the depth of the crucible ranges from 20 to 36 in., commonly about 30. In order to reduce the amount of lead necessary to fill the crucible—which runs from 20 to 40 tons—the walls of the crucible are sometimes sloped in at the sides abruptly, and in certain cases the entire back half of the crucible is bricked solid.

The Arents Siphon lead tap, an aperture through the side wall of the crucible, consists of an inclined square channel (about  $8 \times 12$  in. in cross-section) leading from the bottom of the crucible side wall inside to the top on the outside. At its top, outside the furnace, the channel is enlarged into a dish-shaped basin, the lead well. This tap is placed either at the middle of one of the sides, or preferably, a little toward the front of the furnace. When the furnace is running, the crucible should remain full, or nearly full, of lead, and the lead in the well stands higher on account of the pressure of the blast and the weight of the charge. The discharge of the lead basin is at a level from 4 to 10 in. above the top of the crucible. The furnace man keeps the lead in the basin at a height which maintains the lead in the crucible at the top of the hearth, gaging this by actual experience in tapping. Ordinarily, the furnace man will close up the lead discharge periodically in order to force the lead in the crucible to rise to a level where some begins to run out with the slag, so that he may know that all speiss, matte, and zinc mush has been cleaned out of the furnace when the furnace slag is tapped to a blow.

With charges running high in lead,—30 to 45 per cent—the lead overflows continuously from the well into a suitable lead kettle at the side of the furnace; with the more common 10 to 15 per cent of lead on charge, it is tapped at intervals.

**Handling Ores and Products.**—The blast furnace may be considered as the objective point on which turns the entire transportation system and flow sheet of the plant. The receiving and disposing of raw materials—fluxes, fuels, ores—for the blast furnace, and the disposal of its waste, intermediate, and primary products, form part of the general arrangement of the whole smelting plant, involving also the sampling and storing of materials, roasting and preparing smelting charges, and the disposition of power, water, and other necessary factors. All this involves an engineering problem of considerable magnitude, detailed mention of which is outside the scope of the present discussion. In other sections of the present volume will be found treatments of sampling, fuel, roasting, power, fume collection, slags, and other phases of smelting procedure which are more or less common to reduction plants for all metals.

Briefly stated, the products of the lead blast furnace are disposed of as follows:

1. *Lead.*—Crude lead from the Arents siphon-tap basin is usually transferred to a drossing kettle of some 20 to 40 tons capacity, where it is freed from impurities held in suspension or solution. This is accomplished by “poling” (mechanical stirring of liquid lead by means of compressed air or steam). The impurities which rise to the surface become slightly oxidized and remain on the surface of the bath, from which they are removed, as dross, by skimming with a perforated disc or huge spoon. Formerly, a green pole was thrust into the lead. The gases and vapors set free stir up the lead and expose new surfaces continually to the air, resulting in the slow oxidizing of Cu, S, As, Sb, Zn, and Fe, which collect on the surface as a dross. The kettle filled with liquid lead is allowed to cool to about 480°C. before it is drossed. After dross is removed, the lead is air poled until the temperature drops to about 360°C., removing constantly the accumulating dross. The temperature is then slightly raised (to about 380°C.) for the taking of “gum-drop” samples (small ladle samples weighing 0.5 assay-ton each) and then to about 425°C. for casting the lead. The dross usually goes back to the blast-furnace charge, after being freed by liquation, or pressing, of much of its occluded lead.

An interesting improvement in drossing methods has recently been patented by Hulst; consisting of stirring fine sulphur into the kettles of molten bullion or lead. This causes the copper to rise to the surface with the dross, as sulphide, leaving the bullion very clean of copper, down to 0.05 per cent and less.

2. *Matte and Slag.*—An imaginary cross-section of the crucible of an operating furnace would show the crucible filled with lead, and floating above the lead, speiss, matte, and slag in the order given. The lead leaves the crucible through the siphon tap, which takes off at the bottom, and the other products are tapped through the tap jacket at the front of the furnace, intermittently, into an external receiver, or forehearth, in which they separate in accordance with their specific gravities, speiss at bottom, matte above speiss, and slag above matte. On top of the normal matte there is usually found a zinc mush which separates with difficulty from both slag and matte.

This zinc mush, inside the furnace, and outside, as well, is the bane of lead furnace men and metallurgists; it is the root of furnace troubles which may vary in intensity from merely unsatisfactory assays (metal losses) to the entire loss of the furnace through freezing, or slagging (mushing) of tuyères. More than any other single factor the solution to the zinc-mush difficulty is to eliminate the possibility of its formation,

by dead roasting the sulphides of the charge. Zinc combined with sulphur spells trouble, zinc combined with oxygen is handled and slagged with comparative ease. During the last five or ten years, as the zinc burden at many of the lead plants has increased to heavy proportions, there has been intensive, skilled application to the problem of handling this troublesome element in matte and slag. The solution of the problem has rested largely in so perfecting and extending the roasting operation that practically no sulphide sulphur is left in the charge. With the sulphur content of roasted ore now regularly reduced to from 2 to 3 per cent, it is found at many plants that no matte or mush is produced as a furnace product, the slag itself taking care of the small amount of sulphur that reaches the smelting zone of the furnace.

At virtually every lead-smelting plant of size, this zinc factor has been steadily creeping up as a difficulty and menace during every one of the past five years, as lead ores from constantly deeper zones have been brought to the surface, to be concentrated by flotation. It is proper to say that the aim of lead metallurgy for the past five years has been chiefly to cope with the ever-increasing volume of fine zinc-bearing materials which have been delivered to the smelters by these flotation mills. At present (1925) the art of flotation has moved on into a notably successful stage of selective work, whereby the zinc and lead of complex ores are separated into much cleaner products. This accomplishment is greatly relieving the zinc burden of the lead metallurgist.

As indicated above, better roasting (sintering) has been the largest single factor in meeting the zinc situation. There are two other points in the blast-furnace manipulation of zincy lead charges, that, although not so generally known, are recognized at certain plants as of almost equal importance in combatting zinc troubles. At Namtu, Burma,<sup>1</sup> where slag zinc runs up to 30 per cent ZnO, it has become recognized that zinc troubles are not always sulphur troubles; this plant is more inclined to say that some zinc troubles are sulphur troubles. Some of the most troublesome work on record at the Namtu furnaces occurred when the physical condition of the sinter was quite up to the average, with sulphur only 2 per cent; furnace clean; coke good; and when the analysis of the resultant slag was in line with their best types. Trouble appeared because, although the zinc and the iron were in the charge in the correct proportions, they were not there in the correct condition. It is one thing when the iron necessary to satisfy the slag demands of the zinc exists in the charge in intimate association with the zinc and when also, a comparatively small amount of slag material has to be made to carry the zinc in the concentrate as at Broken Hill and the Coeur d'Alene; it is another, and much more troublesome, matter when the iron requisite for a heavy zinc charge has to be supplied almost entirely, as at Namtu, by the addition of limonite, and to obtain satisfactory combination, a considerable heat reaction is required. At Namtu, it is also to be noted that a slag fall of 2:1 is obtained by the amount of slag which has to be formed to carry the zinc, even when this slag contains 30 per cent ZnO.

At Cockle Creek, N. S. W.,<sup>2</sup> control of zinc troubles had been secured, prior to the shutting down of this plant of the Sulphide Corporation, by smelting methods which were almost unique in lead blast furnace practice. A combination of high ore column (26 to 28 ft.) and high blast pressure (approximately 70 to 75 oz.) maintained an intensity of temperature at smelting zone and a drive of the furnace that resulted in remarkable freedom from zinc accretions and troubles, and gave slags carrying well under 1 per cent lead, with no unusual losses in any direction.

Where matte is still made in appreciable quantities, large movable forehearth (about 8 by 4 by 4 ft.) receive the stream of slag and matte tapped from the furnace breast. The matte is trapped, and accumulates in the forehearth, while the slag

overflows from the top. At intervals the matte is tapped through the side. The waste slag pots are hauled away by power and slag disposed of either by pouring over the dump or into a granulating apparatus. The latter is becoming more frequent of late, as modern practice is demanding granulated slag as a diluent for blast-roasting charges.

Formerly, all shells and crusts from waste slag pots were brought back to the blast furnace for resmelting, because of enrichment of lead and silver in the shell, fluxing requirements, and beneficial effect on the blast-furnace charge, but the practice of recent years tends to discontinue the resmelting of slag shells, substituting therefor the resmelting of receiver (or forehearth) bottoms. Two forehearth in series are becoming popular, with consequent throwing away of the entire contents of the slag pots. In a few instances the slag-matte mixture tapped from the blast furnace is transferred to a small reverberatory settling furnace from which matte and slag are intermittently removed.

The matte contains silver, gold, lead, and copper, and must all be retreated. It is crushed—at some plants granulated from the forehearth—mixed with the roaster charges, and desulphurized, before being returned to the blast furnace. Or, it may be concentrated (by “matte smelting”) into a smaller amount of copper-rich matte which is sold to copper works. Or leady-copper mattes may be converted, with or without the addition of siliceous fluxes, in a manner similar to the standard treatment of copper-iron mattes, by forcing air in small streams through the side of an iron vessel lined with basic refractory material, into the molten matte at a temperature of 1100 to 1200°C., oxidizing the Fe, Pb, and S, and recovering the Cu, As, and Au, as metal. The oxidized Fe is slagged, and the Pb is partly slagged, partly volatilized. Slagged Fe and Pb, as well as volatilized Pb, are subsequently retreated in the blast furnace.

3. *Fume and Dust.*—Hoods are placed everywhere around a blast furnace where fumes arise, the pipes from all hoods leading to a main flue and exhaust fan which deliver to a bag house or Cottrell plant. The gases and dust issuing from the top of the furnace, combining with the fumes from the tapping floor, travel through flues and chambers in which they drop most of their dust, and then to special condensation or filtering apparatus. The methods for recovery of flue dust and fume at lead smelteries and refineries may be classed as dry, wet, and electric. In another section of the present volume the subject of dust treatment is discussed in greater detail.

**Chemistry of the Lead Blast Furnace.**—The charge—ore, flux, and coke—fed at the top of the furnace, is subjected as it descends through the shaft in about 8 hr., at gradually increasing temperatures, to chemical reactions and physical changes which transform it into lead bullion, speiss, matte, slag and gases. The two processes principally involved are reduction and precipitation, and incidentally sulphurization, at temperatures ranging from 1100 to 1200°C. at the tuyère level, to 150°C. at the throat.

The principal reducing agents are C and CO. The carbon, supplied by the coke (normally 8.5 to 13 per cent of charge) acts upon metallic oxides as soon as temperature rises to a point where its affinity for oxygen is greater than that of the metal that is combined with the oxygen, this action beginning at about 400°C. The products of oxidation are CO<sub>2</sub> and CO, the former resulting if the metallic oxide is easy of reduction, say below 1000°C., the latter if the oxide is difficult of reduction, perhaps above 1000°C. The reducing action of CO, which begins at about 200°C., increases with temperatures up to about 1000°C., beyond which point it falls off rapidly.

The principal agent of precipitation is iron. Other metals act as precipitants also, in conformity with their affinities for sulphur. Each metal will displace from sulphides



other metals, whose affinity for sulphur is weaker, according to Fournet in the following order:

Cu — Fe — (Co — Ni) — Sn — Zn — Pb — Ag — Hg — Au — As — Sb

The more recent work of Schütz places the series in slightly different order, as follows:

Mn — Cu — Ni — Fe — Sn — Zn — Ag

Precipitation, or decomposition of sulphide by metal, begins at about 900°C., and is at a maximum at tuyère level, where the furnace temperature is around 1200°C. The precipitation reaction is reversible, however, and the complete decomposition of the metallic sulphides by iron is thus counteracted to some extent.

**Descending Ore Charge.**<sup>1</sup>—In considering the changes in the descending ore charge, it is convenient to distinguish four zones: the zone of preparatory heating, 100 to 400°C.; the upper zone of reduction, 400 to 700°; the lower zone of reduction, 700 to 900°; and the zone of fusion, 900 to 1200°. There is no sharp line of demarcation between the zones, one passing over into the other; the reactions beginning in one zone may be finished only in the next or perhaps even the second lower down. The process of heat interception is continuous from the tuyères to the throat, or from 1200 to 100°C.

1. *Zone of Preparatory Heating* (100 to 400°C.).—The charge fed into the furnace first gives up its hygroscopic water, then that which is chemically combined. Clayey material, limonites, and some other hydrates give up at 400°C. only part of this water. The evaporation of water absorbs heat and thus assists in keeping the top of the furnace cool.

2. *Upper Zone of Reduction* (400 to 700°C.).—The decomposition of hydrates continues, the dissociation of carbonates and of some sulphates begins. The reducing effect of CO, which theoretically begins at 200°C., becomes noticeable only at about 400°, and increases with rise of temperature up to about 900°. It will, therefore, be an active agent in reducing PbO completely to Pb, and PbSO<sub>4</sub> partly to PbS; it will also start the reduction of Fe<sub>2</sub>O<sub>3</sub>. The C of the coke, which begins to act reducingly at about 400°C. and increases as the temperature rises, will change PbO completely into Pb, and PbSO<sub>4</sub> partly into PbS; it will assist CO in its reduction of Fe<sub>2</sub>O<sub>3</sub>, and will transform CO<sub>2</sub> of the gas current into CO. There will further take place reactions of PbSO<sub>4</sub> and PbO and PbS, setting free Pb and SO<sub>2</sub>.

3. *Lower Zone of Reduction* (700 to 900°C.).—The reactions started in the preceding zone continue and are in part completed; the effect of C becomes more marked than that of CO. The CaSO<sub>4</sub> in blast-roasted ore as well as BaSO<sub>4</sub> in raw ore are more or less reduced to CaS and BaS to be dissolved later on mainly by the slag. The dissociation of carbonates is about completed, CaCO<sub>3</sub> at 910°. The union of SiO<sub>2</sub> with unreduced PbO and PbSO<sub>4</sub> begins, as does the decomposition of PbS, PbAs<sub>2</sub>, PbSb<sub>2</sub> by Fe; sulphurization of Cu begins about at the same temperature. Matte of eutectic composition begins to soften. Everything is prepared to be liquefied and to bring to completion the chemical processes.

4. *Zone of Fusion* (900 to 1200°C.).—The reductions of oxides, including ZnO, and decompositions of sulphides are completed; ascending Zn vapor is oxidized and sulphurized. Lead reduced in the upper parts of the furnace trickles through the charge, picking up Ag on its way, and acting possibly upon lead arsenate and antimonate; it joins the Pb set free lower down from PbS, PbAs<sub>2</sub>, PbSb<sub>2</sub>, and continues to take up Ag. The sulphides of eutectic composition, which softened higher up, become liquid and dissolve other sulphides to form matte with a melting point lying below that of slag formation. The slag components SiO<sub>2</sub>, FeO, and CaO form a slag of lowest formation temperature and this, trickling downward, dissolves the remaining SiO<sub>2</sub>,

<sup>1</sup> HOFMAN, H. O., "Metallurgy of Lead," p. 343, 1918.

FeO, CaO, as well as other bases, such as  $\text{Al}_2\text{O}_3$ , ZnO, etc. Scorified PbO is set free and reduced by C to Pb. The three main products—lead, matte, and slag—settle in layers according to their specific gravities; lead passing downward through slag and matte robs these of some precious metal; matte in a similar way removes Pb, Cu, and Ag from the slag; at the contact planes of the products, interchange of components takes place to a moderate degree with a tendency to collecting sulphide in matte, and metal in lead. The lead passes off through the lead well; speiss, matte, and slag are tapped into the forehearth, from which slag overflows into a waste-slag pot or granulating apparatus, and speiss and matte are tapped periodically into suitable receivers.

An innovation in the feeding of lead blast-furnace fuel that has had some little attention among American metallurgists in these last two or three years, and one which considerably alters the normal chemistry of the furnace, is the introduction of powdered coal through the tuyère orifices, as a substitute for a portion of the coke normally charged at the top of the furnace. Although this procedure has been used

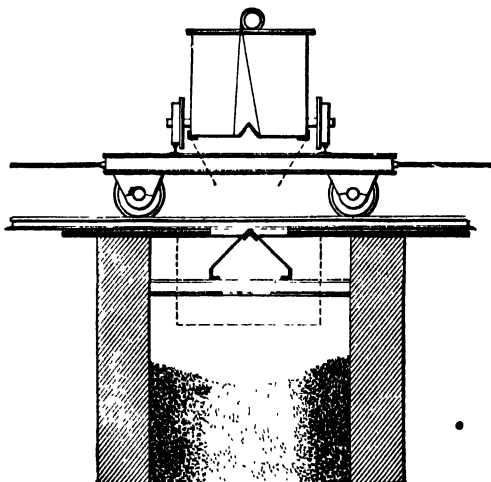


FIG. 5.—East Helena feeder with Dwight spreader.

with a considerable degree of success in recent years in copper blast furnaces in Kosaka, Japan, and Cerro de Pasco, Peru, its utility in the lead furnace is still of uncertain degree. It has been found possible at Midvale, Utah, to substitute up to 30 per cent of the coke normally used, by powdered coal, thereby effecting some saving in the fuel costs, and obtaining better reduction and cleaner slags in a majority of instances. A slowing up of the lead furnace results, however, which has led the balance of metallurgical opinion to view the worth of the procedure as doubtful. One plant only has been seriously attempting the practice, and at present the use at this point is held up, pending the settlement of patent entanglements. The method has many possibilities, without question, which have not yet been fully demonstrated; it is conceivable that the difficulties of slower furnace speed may be overcome by coarser, and specially prepared, sintered charges, and other methods of control.

**Mechanical Feeding of Charge.**—The metallurgical and practical success of a blast-furnace operation depends as much on a proper physical condition of charge and its accurate distribution in the furnace shaft, as it does on the actual con-

stituents of the charge and their accurate calculation by the metallurgist in control. One of the greatest steps in the advance of lead blast-furnace work occurred when the old hand-feeding methods were replaced by mechanical feeding, about 1900, along lines developed by A. S. Dwight in Montana. This mechanical feeding system, and the general adoption of blast-roasted and sintered products in the ore charge, constitute the major improvement in the smelting of lead that has been developed in many years. Tonnages and metallurgical recoveries have been enormously benefited by this step, which has almost revolutionized the art.

Charge components, made up of ore, flux, fuel, and secondary products, vary greatly in size. In an ideal assortment of sizes, about one-third of the charge would in pieces from 5 to 2 in. in diameter, one-third from 2 to  $\frac{1}{2}$  in., and the remaining third from  $\frac{1}{2}$  in. down.

A coarse charge is preferable to a fine one, as the ascent of gases is more uniform; if too coarse, however, the gases pass up and away too quickly and do not get in their proper work on the descending charge. A fine charge obstructs the flow of gases to

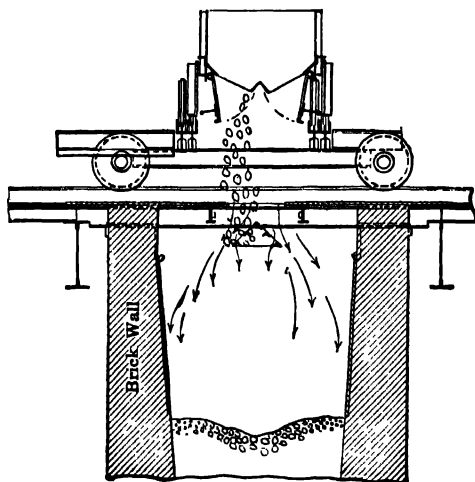


FIG. 6.—Dwight-Norton spreader.

too great an extent, and the gases tend to break through at various points in the form of blow holes, which upset the chemistry and operation of the furnace completely and cause loss by carrying off dust and fume. In furnace work there is always a danger of fines trickling through the coarser parts of the charge and reaching the smelting zone in a crude state, chilling the furnace and even clogging the tuyères. In modern smelting, with charges made up largely of blast-roasted materials, the fines have been reduced to such an extent that they seldom cause trouble.

In general, the courser parts of the charge must be placed toward the center of the shaft, and the finer material toward the side walls. The ascending gases have a tendency to hug the sides of the shaft, and their passage must be adjusted by charge distribution, so that the gas current will ascend evenly and uniformly over the whole area of the smelting column. The method of mechanical feeding developed at East Helena by Dwight in 1900 is at present in use at the majority of plants, in more or less modified forms. The principle used is shown in Fig. 5.

The contents of the charge car (4 tons) drop onto an A-shaped spreader which throws everything toward the sides of the furnace shaft where the bulk of the fines remain, while the coarser parts roll down the inclined surface or trough of the descending charge and gather along the center axis. To prevent carrying this segregation of coarse and fine too far, a modification of the Dwight spreader was adopted by W. W. Norton at Murray, Utah, in which the A-shaped spreader, instead of being a solid casting was made up of several parts separated by open spaces, or slots, as shown in Fig. 6. The charge, on dropping onto this spreader, is not all deflected toward the side walls, but a portion falls directly through the slots and lands in the center of the furnace. A satisfactory distribution of charge results, much fine with some coarse along the sides, and much coarse with some fine along the center.

With charges in recent years made up so largely of blast-roasted product, and the consequent greater smelting speed of the furnace, there is less danger of the heat creeping up in the furnace, and there is now a tendency to try to distribute coarse and fine more evenly through the furnace than of old.

A few years ago there was, at a few of the American plants, a revival of the old Darby tube, or thimble, method of feeding charge and removing gases at furnace top, this being the method in vogue at the Australian smelteries. This contemplates a pipe or flue suspended in the center of the furnace, for the withdrawal of gases, around which the charge is fed. As the charge sinks to the bottom edge of the pipe, the coarse rolls ahead of the fines into the trough of the furnace, resulting in much the same distribution as is secured with the Dwight spreader.

There is now a general tendency at American plants to get away from this Australian, or Darby method, and to return to the Dwight system of charge distribution.

**Smelting Lead Ores in the Reverberatory Furnace.**—Until within comparatively recent years the smelting of sulphide lead ores in the reverberatory furnace was very common, especially in England, Belgium, and Austria. Since blast roasting has come into general use, however, reverberatory work has become nearly obsolete. In the United States there were in operation in Missouri in 1877, fifty-six reverberatory furnaces, in 1914 only four. •

The process involved was the roast-reaction or air-reduction process, based on the reactions between  $PbS$ ,  $PbO$ , and  $PbSO_4$  at temperatures below  $1000^{\circ}C$ ., which set free  $Pb$  and  $SO_2$ . The precipitation process, based on the decomposition of  $PbS$  by  $Fe$ , was formerly in operation with raw lead ores in France and at Chicago, also with roasted ores in Cornwall. The precipitation process, as a separate procedure, has been given up because of high cost and heavy loss of metal.

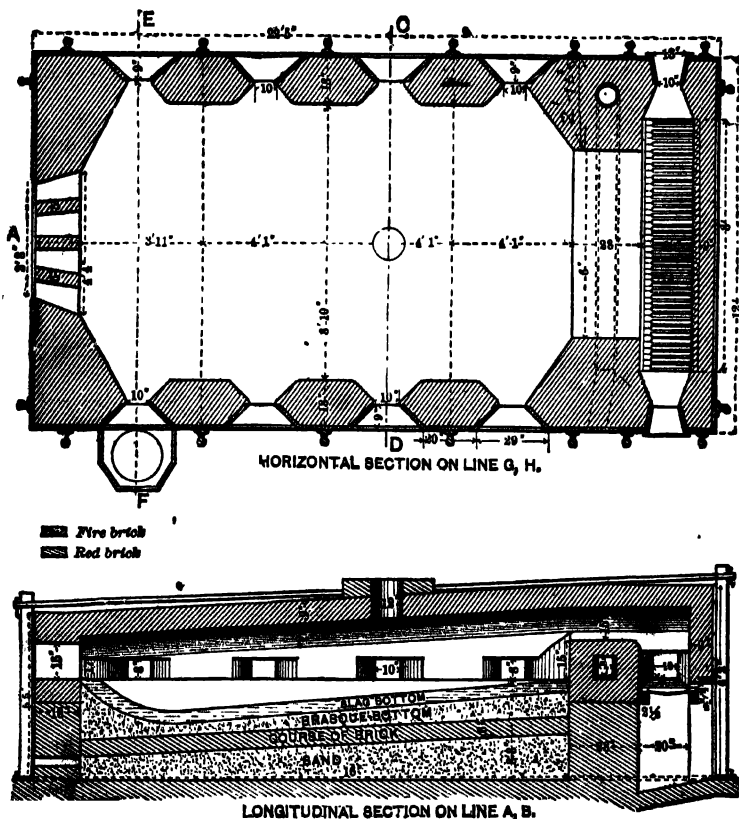
The roast-reaction process in the reverberatory furnace involves two operations, oxidation and reduction, one following the other closely, and both being several times repeated. The finely crushed ore, spread in a layer 4 in. deep on the hearth, is heated gradually to a dull red ( $500$  to  $600^{\circ}C$ .). The roasting is carried on in such a way that only a part of the  $PbS$  is converted into  $PbO$  and  $PbSO_4$ , the rest remaining undecomposed. The second step of the operation is that of raising the temperature to about  $800^{\circ}C$ . so that the oxygen compounds may react on undecomposed sulphide. The resulting metallic lead runs down the inclined hearth and collects in a basin, the  $SO_2$  escapes into the flue, and the residue remains on the hearth. The temperature must remain low during this reduction period, so that the charge will not melt, but will remain in a pasty condition. The reactions are imperfect if the ore be melted.

It is impossible to roast a large amount of lead ore uniformly in one operation. The first reaction that takes place on raising the temperature will not extract all the lead. The residue will contain rich  $PbS$ , with some lead oxide, lead sulphate, and lead silicate. The temperature is lowered, air admitted, and a second roasting takes place,

followed by a second reduction. This cycle is several times repeated before the bulk of the lead is extracted. With each successive reduction, the temperature must be raised, slightly, as the amount of lead diminishes. To counteract the melting of the charge, slaked lime is added. Toward the end of the process there will not be enough  $PbS$  left to react on the  $PbO$  and  $PbSO_4$ , and to reduce these, coal is mixed in. Each successive operation is of shorter duration than the preceding one, and the metallic lead obtained is each time a little less rich in silver.

The products of reverberatory smelting are:

1. *Lead*.—If clean enough this can be rendered fit for market by simply liquating and poling; if carrying arsenic, antimony, or copper, refining must be resorted to.



FIGS. 7-8.—Silesian reverberatory furnace.

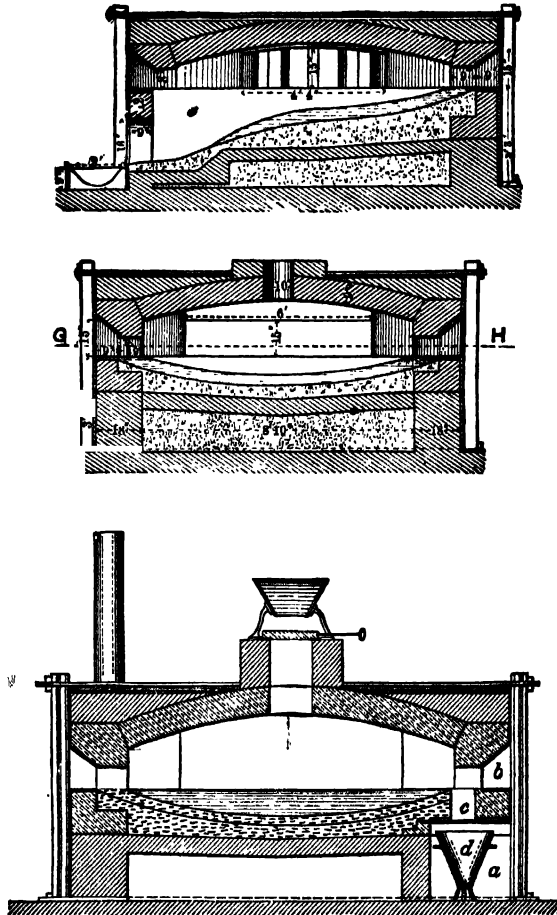
2. *Gray Slag*.—This is a more or less matted mixture of lead ( $PbS$ ,  $PbO$ ,  $PbSO_4$ ,  $PbSiO_3$ ), gangue, cinders, and lime, with some silver. It is crushed and smelted in the blast furnace.

3. *Flue Dust*.—This consists mainly of oxidized compounds and is worked in with subsequent charges, shortening the time required for roasting. If very impure, it is smelted in the blast furnace, along with the gray slag.

4. *Hearth Bottom*.—This consists of hearth material impregnated with metal. It is worked up in same manner as the residues.

## LEAD

**Limitations of Roast-reaction Process.**—To be suited for the reverberatory furnace an ore must be a rich galena, or a mixture of galena and carbonate, that does not contain less than about 60 per cent Pb, 70 per cent being preferable. It may not contain more than 4 or 5 per cent  $\text{SiO}_2$  and its content of blende, pyrite, chalcopyrite, calcspar, and barite must be low. The process takes heavy fuel and much skilled labor



CROSS SECTION THROUGH DOOR NEAR FIRE BRIDGE

FIGS. 9-11.—Silesian reverberatory furnace. (a) Opening beneath drawing door, b, receive slag pot, d. (c) Drawing opening. (g) Stationary iron flue pipe. (h) Telescopic stack, lowered to position k when lead is to be tapped.

**Classification of Reverberatory Methods.**—Reverberatory procedure varies widely in different countries, three distinct methods of reverberatory work being developed—Carinthian, English, and Silesian. Some of the principal plants work toward the object of extracting as much lead as possible in the reverberatory

(Carinthian and English), while others supplement the reverberatory by the blast furnace, taking out only a major portion of the lead in the former. The rich residue from the reverberatory, smelted in the blast furnace, permits a higher total extraction (Silesian). Then, some establishments roast the ore slowly at a low temperature, thereby obtaining a maximum recovery of lead (Carinthian and Silesian), while others conduct a hurried, high-temperature roasting, aiming to save time and labor at the expense of metal (English). Reverberatory furnaces vary in form and size also.

The Carinthian method is distinguished by the smallness of the charge, slow roasting, low temperature of all operations, and the extraction of all the lead in the reverberatory. The hearth is inclined toward the flue and the lead collected outside the furnace.

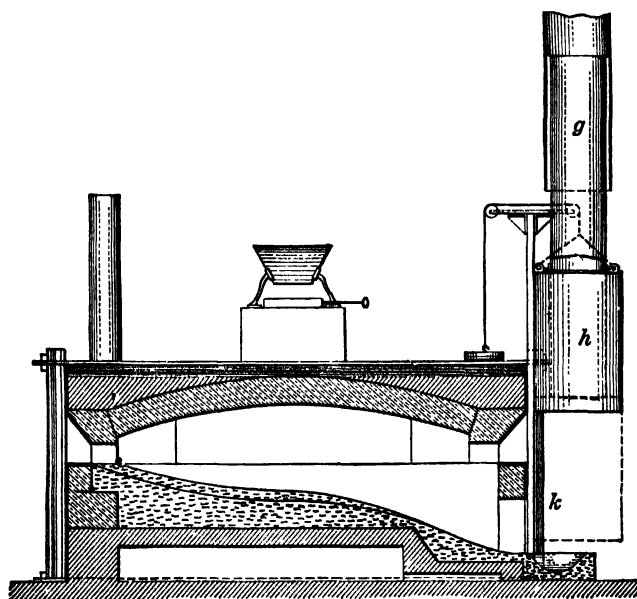


FIG. 12.—Silesian reverberatory furnace.

The English method is marked by a large charge, quick roast, high temperature throughout, and extraction of all the lead in the reverberatory. The hearth slopes toward the middle of one of the sides, and the lead collects inside the furnace, being tapped at intervals into an outside kettle.

The Silesian method is characterized by a large charge, slow roasting, and a low temperature, the lead being only partly recovered in the reverberatory, which is supplemented by the blast furnace. The hearth is inclined toward the flue, beneath which the lead is collected and tapped at intervals into an outside kettle.

The Silesian furnace (Tarnowitz) is shown in Figs. 7, 8, 9, 10, 11, 12.

The main data on the principal reverberatory furnace plants, assembled by Hofman, 1918, is shown in the following table:

# LEAD

EXAMPLES OF SMELTING IN REVERBERATORY FURNACES

Items	Carinthian method				English method			Silesian method	
	Raibl, Carinthia	Engis, Belgium	Granby, Missouri	South-west Missouri	South-east Missouri	Holywell, Flintshire	Stiper-stones, Shropshire	Desloge, Missouri	Tarnowitz, Silesia Old furnace New furnace
<i>The furnaces</i>									
Hearth, length.....	11'	6' 6 $\frac{3}{4}$ "	9'	9'	10'	12'	9' 9"	16'	16'
Hearth, width at bridge.....	5'	4' 3 $\frac{1}{2}$ "	3' 2"	3'	2' 6"	3' 6"	4'	6'	6'
Hearth, width at middle.....	5'	4' 4 $\frac{1}{4}$ "	3' 2"	3'	4'	9' 6"	3' 6"	11'	8' 10"
Hearth, width at flue.....	1'	2' 3 $\frac{1}{2}$ "	3' 2"	3'	2'	4'	3' 3"	8"	4' 4"
Hearth, thickness of bed.....	6"	1' 5 $\frac{1}{4}$ "-2' 8 $\frac{1}{4}$ "	6"	6"	2"-10'-26"	2"-10'-26"	4"-18"-30"		4' 4"
Hearth, life of bed, weeks.....	4-5	6							13
Hearth, inclination to flue or side.....	21° F.	17° F.	18° F.	-F.	-F.	20° S.	24° S.		27 $\frac{1}{2}$ ° F.
Grate, length.....	7'	3' 7 $\frac{1}{4}$ "	5' 6"	6' 6"	3'	4' 6"	4' 6"	8'	8'
Grate, width.....	1' 3 $\frac{1}{2}$ "	1' 6"	2' 6"	2' 6"	2'	2' 6"	2' 6"	1' 3"	1' 8"
Grate, depth below top of bridge.....	1' 3 $\frac{1}{2}$ "	3' 7 $\frac{1}{4}$ "	8"-30"	6"		2' 9"	1' 4"		28"
Bridge, width.....	5 $\frac{1}{2}$ "	1' 3 $\frac{1}{2}$ "	30"	30"	21"	24"	24"		72"
Bridge, length.....	3' 7 $\frac{1}{2}$ "	3' 11 $\frac{1}{2}$ "	30"	6"	24"	42"	48"		15"
Bridge, height above hearth.....	4-5'	none	14"		6"-8"	12"	12"		12"
Roof, height above bridge.....	9"	8 $\frac{1}{2}$ "	14"		6"-8"	10' 1"	10' 1"		17"
Roof, height above hearth at flue.....	12"	2' 3 $\frac{1}{2}$ "	14"		6"-8"	16"	20"		4(15" X 20")
Flue (leading to chimney), size.....	1' X 1' 3 $\frac{1}{2}$ "	8 $\frac{1}{2}$ " X 2' 3 $\frac{1}{2}$ "	8" X 12"		12" diam.	12" X 10"	12" X 12"	2(16" X 18")	Similar to new furnace.
Chimney, inside size.....	1' 6" X 1' 8"	1' 3" X 1'			12" diam.	10" X 10"	11" X 12"	42" diam.	
Chimney, height.....	20'			20'	15'	3' X 3' 6"		55'	
Grate area, ratio to hearth area.....	1:6	1:5.25	1:2.0	1:1.66	1:5.4	1:8	1:6.6	1:7.3	1:10
Grate area, ratio to section of chimney.....	1:0.14	1:0.47			1:0.13	1:0.93		1:0.40	

\* Kemp, *School of Mines Quarterly*, 1887-88, II, p. 212. 1 Height of roof above grate, 38'.



EXAMPLES OF SMELTING IN REVERBERATORY FURNACES.—(Continued)

Items	Carinthian method				English method			Silesian Method	
	Raibl, Carinthia	Engl., <sup>1</sup> Belgium	Granby, Missouri	South-west Missouri	South-east Missouri	Holywell, Flintshire	Stiper-stones, Shropshire	Desloge, Missouri	Tarnowitz, Silesia Old furnace      New furnace
<i>Work done</i>									
Charge, weight in pounds.....	370-430	1,375	1,500	1,500	.....	2,350	2,350	3,325	4,400
Charge, assay, per cent. lead.....	70	76	.....	.....	.....	75-80	77 5	70	70-74
Charge, thickness on hearth.....	1½"-1½"	about 3"	.....	.....	.....	15½"	3½"-4½"	.....	3"-4"
Operation, length in hours.....	10-12	12	12	9-11	.....	6	7	8	12
Men, number in 24 hr.....	1-5	4	2	2	.....	6	4	6	6
Gray slag, amount in pounds.....	95	275	.....	.....	.....	288	.....	906	2,475
Gray slag, per cent. of charge.....	24	12	.....	.....	.....	12	.....	27	15
Gray slag, assay, per cent. lead.....	4	17-20	55	.....	.....	55	.....	38	38.8
Of lead charged, recovered per cent., in bags	93	92.5	.....	.....	.....	81	88	54.4	87.5
Recovered from gray slag and flue-dust.....	.....	2.3	.....	.....	.....	8	.....	10	9.3
Total loss in lead.....	7	5.2	.....	.....	.....	11	12	91	3.21
<i>Outlay for labor, fuel and material per ton of ore of 2,000 lb. avoirdupois</i>									
Labor, hours.....	90	61	36 aver.	20	.....	15	12	8.4	11
Fuel, charcoal, pounds.....	.....	.....	.....	.....	.....	.....	.....	.....	9
Fuel, bituminous coal, tons.....	.....	1.10	.....	.....	.....	0.57-0.76	0.56	0 8-0.9	0.46
Fuel, wood, cords.....	.....	.....	.....	0.83	.....	.....	.....	.....	.....
Material, lime, pounds.....	1.00	.....	1.10 aver.	.....	.....	.....	.....	26	20

<sup>1</sup> Includes smelting residue in the blast furnace.

Hofman.

**Smelting Lead Ores in the Ore Hearth.**—The ore hearth has come back into an important position in the lead industry during the present century. It is an ancient method, with operating principles which may be said to be intermediate between a reverberatory and a blast furnace. At first the only method for working low-silica, high-grade, galena ores, it passed into disuse and became largely replaced by the reverberatory furnace, but the reverberatory has given way in recent years, with the advent of the bag house and Cottrell electrolytic processes for the collection of fume and dust, and the ore hearth, in modern, mechanical form, has taken a new lease of life. In 1914, there were in operation in Missouri alone seventy-five ore hearths (hand operated) with an annual capacity of 230,000 tons of galena concentrate; by 1923, the Newnam mechanical ore hearth had replaced all of the hand hearths on the American continent, and about seventy-eight of these furnaces are in operation with a capacity of 490,000 tons annually.

Plants have also been erected, and are at present in operation, in Canada, England, Spain, and South America, treating not less than 60,000 tons. The total tonnage being treated over the Newnam hearth was about 550,000 in 1924, a figure which is increasing.

An ore hearth is, essentially, a low fireplace surrounded by three walls, with one or more tuyères at the back. It is invariably made of cast iron. In the front there is a cast-iron "work plate," with a groove to carry off the reduced lead into a kettle. There is usually a partial front wall composed of a thick bar of iron, but often the front is simply a dam formed of ashes and powdered galena which is impervious to melted lead. The sides and back must be of iron in order to admit of chipping off the half-fused masses of slag which constantly adhere to them; they may be cooled simply by radiation from large, heavy castings (Scotch hearth), by a current of air (Rossie hearth), by a water box (American water-back hearth), or by both air and water boxes combined (Moffet-Jumbo hearth). These differences may conveniently be taken as indicating the four distinct modifications of the hearth process, though the manipulation is much the same in all. The Newnam mechanical hearth, water cooled, is, of course, a fifth type.

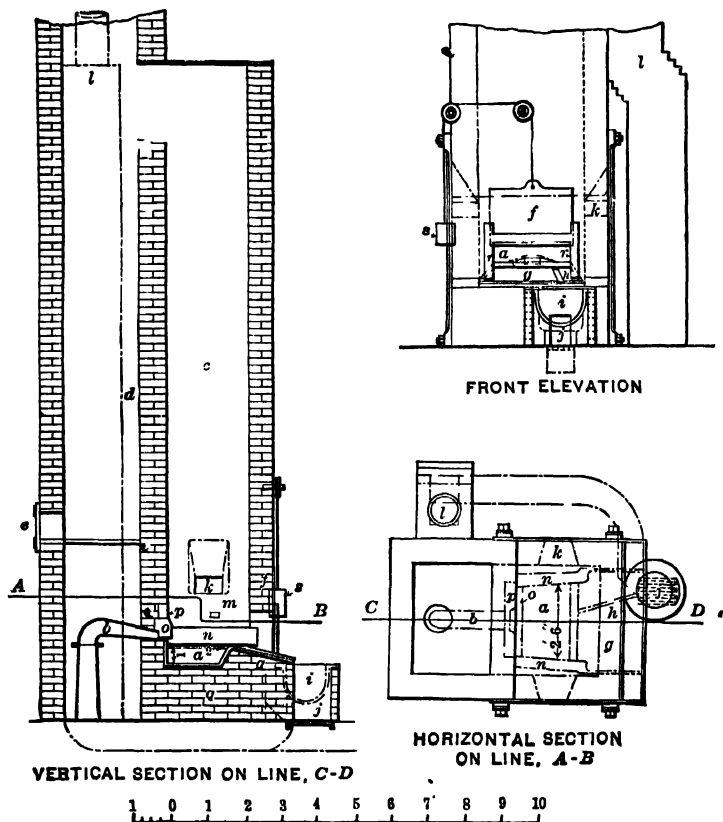
The process carried on in the ore hearth is mainly the roast-reaction process, resembling that of the reverberatory furnace, but differing in the respect that roasting and reduction go on simultaneously, and that there is considerable direct reduction of lead oxide to metal by the carbon of the fuel. The charge—ore and fuel—floats on a bath of molten lead; the  $PbO$  and  $PbSO_4$  react on undecomposed  $PbS$ ; some  $PbO$  is reduced by  $C$ ; and the metallic lead trickles through the charge to the bottom, overflowing into an outside kettle.

The character of the ore to which the hearth process is adapted, is determined by much the same limitations as for the reverberatory furnace. These limitations, however, are even more strict than for the reverberatory, the  $Pb$  content (usually 70 per cent) should not be less than 65 per cent, the ore should be coarser (necessitating preliminary pugging or agglomerating, if too fine), and only low-silver ores should be treated. The latter restriction is due to the fact that much lead and silver is volatilized, under the blast of the ore hearth. With the development of methods of recovery of dust and fume in bag houses and Cottrell plants, these volatilization losses are, of course, greatly reduced.

The ore hearth has one great advantage over the reverberatory—it is quickly started and stopped, without much loss of fuel or heat, and is, therefore, adaptable to the intermittent extraction of lead from small amounts of non-argentiferous ore.

It also consumes less fuel than the reverberatory, but requires purer and higher-grade ore.

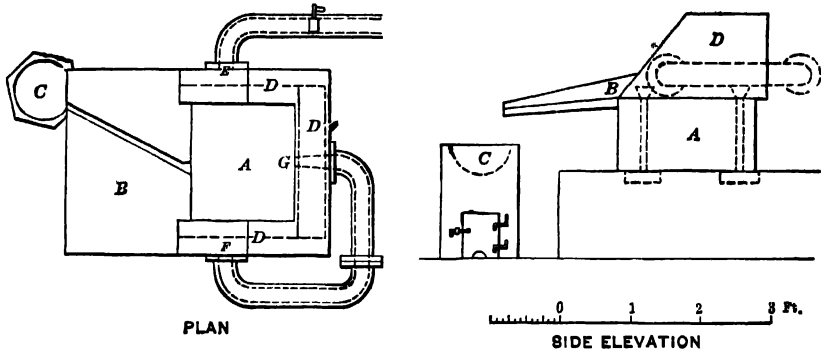
On the non-argentiferous, high-grade lead ores of the Mississippi Valley, the mechanical ore hearth is almost supreme, although one large smelting plant remains still an advocate of the blast furnace as a method of primary treatment. The other two major smelteries are reducing galena concentrates of about 70 per cent grade to bullion and gray slag on mechanical ore hearths, utilizing the blast furnace only as secondary equipment for the smelting of gray slag. Both methods are conducted with high efficiency, and the blast-furnace procedure has ardent advocates, but the high-grade ore of the district is peculiarly adapted to ore-hearth treatment. On ore of 70 per cent



FIGS. 13-15.—Hand-operated ore hearth (English).

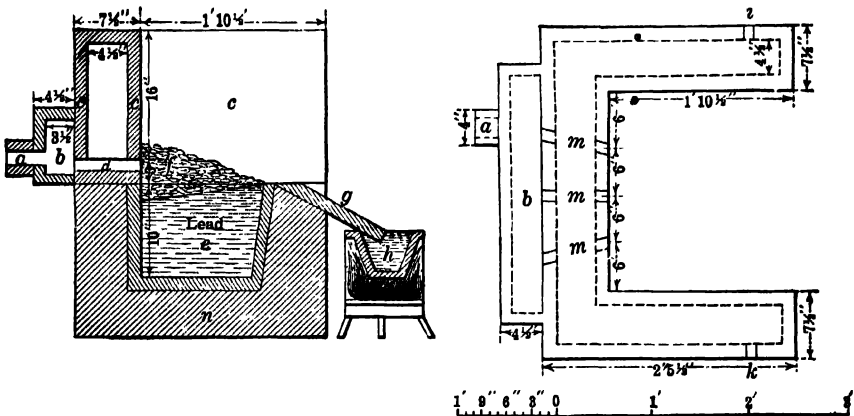
grade, or better, a 65 to 70 per cent lead extraction is obtained, as bullion, on the hearth; if the concentrate is 80 per cent grade, a 90 per cent extraction, or better, is possible, coke requirements being from 3 to 5 per cent breeze. Of the lead charged 15 to 20 per cent is rehandled as bag-house dust and fume, but this is largely  $\text{PbSO}_4$  and  $\text{PbO}$ , which is of immense assistance in the ore-hearth process, which depends on the interaction of galena with the oxide or sulphate to form  $\text{SO}_2$  and precipitate Pb. If there were a sufficient amount of oxidized product present to oxidize all the  $\text{PbS}$ , it would be possible—theoretically—to reduce and recover all the lead in both forms with but little extraneous heat.

About 10 to 15 per cent of the lead goes into a 50 per cent product—gray slag—which must be retreated, and which makes an excellent material for rapid, efficient blast-furnace smelting. The Collinsville, Ill., plant, as will be seen from the blast-furnace table, using Newnam mechanical ore hearths (and blast furnaces for auxiliary treatment), maintains an abnormally high smelting speed on its blast furnaces, 7.9 tons of charge per square foot of hearth (blast furnace) area, due to the easy smelting charac-



FIGS 16 17.—Rossie air cooled ore hearth

teristics of the gray slag which forms the principal constituent of its blast-furnace charge. On the other hand, it is to be noted that the Herculaneum plant with 90 per cent of its blast-furnace charge made up of Dwight machine double-roasted concentrate, and with no ore hearths or gray slag involved, has increased its smelting speeds of late to the figure of 6.6 tons charge per square foot of blast-furnace hearth



FIGS. 18-19.—Original American ore hearth.

area. It has been found that the flotation concentrates of the Mississippi Valley, carrying 56 per cent lead, are not advantageously treated on the ore hearth, but must for maximum economy be double roasted and smelted in the blast furnace.

The products of the ore hearth are similar to those of the reverberatory, with the added product of "browse," a mixture of ore, slag, and fuel, which goes back to the

charge in the ore hearth. The gray slag produced is high in lead and is frequently treated in the slag-eye furnace—a small blast furnace with hot top—where its lead contents are volatilized and then caught in bag houses for use as paint, basic lead sulphate, or “sublimed white lead.”

Being a simple type of metallurgical furnace, the ore hearth shows but little variety in construction or manner of operating. The four early hand-operated forms, shown

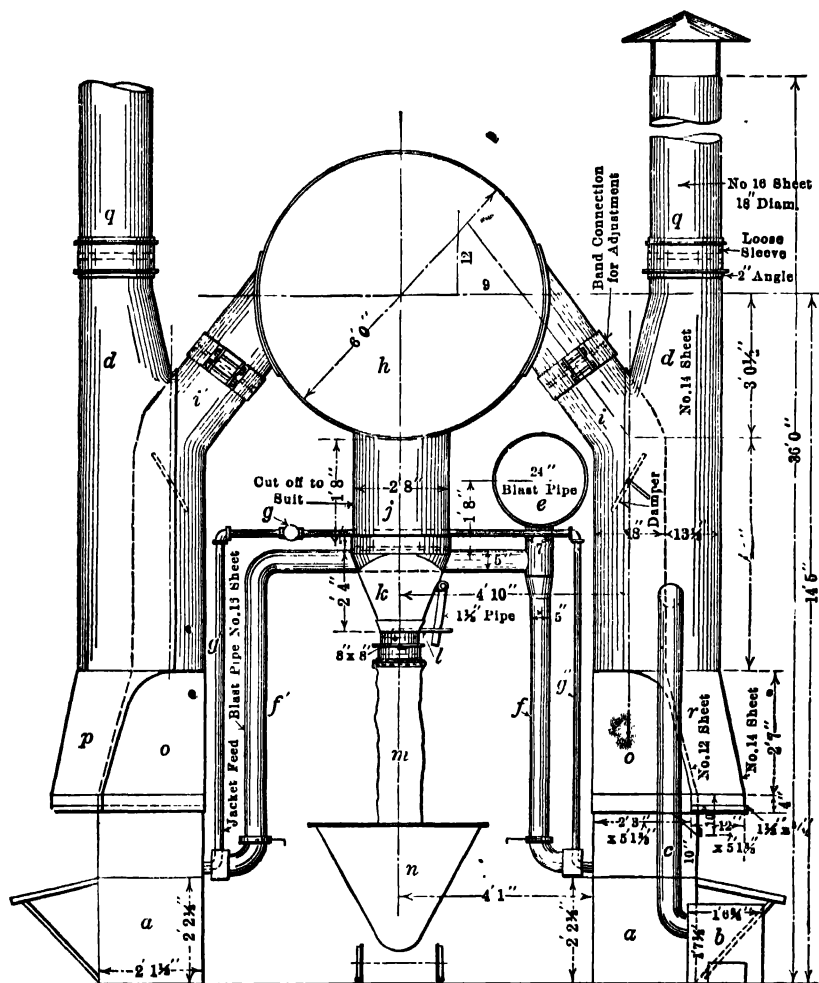
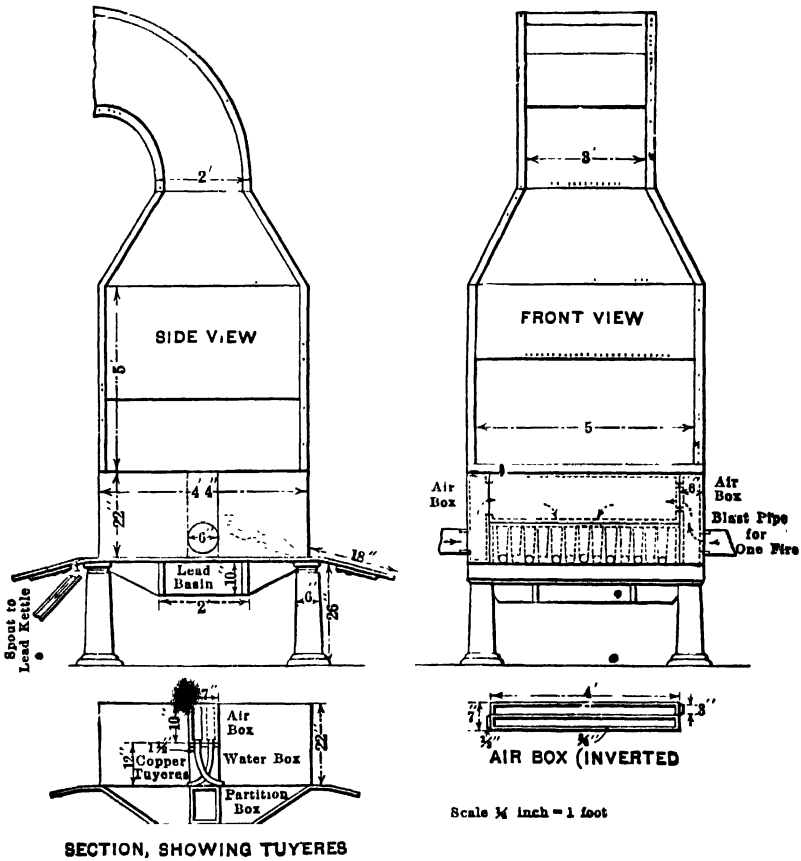


FIG. 20 Modern American ore hearth.

in the accompanying illustrations (Figs. 13 to 24), differ somewhat radically from the mechanical furnace, the Newnam hearth, shown in Figs. 25 to 37.

*Scotch Ore Hearth.*—Figures 13, 14 and 15 show a furnace used in England. The cast-iron box, *a*, set in brickwork *q*, measures 2 ft. (front to back) by 2 1/2 ft. (width). It is 1 ft. deep, and holds about 2 tons of lead. Work stone *g*, an inclined plate, is cast in one piece with the hearth box. Groove *h* leads the overflowing lead to kettle *i*,

heated from fireplace *j*; the gases passing off through a flue into chimney *l*. On either side of the hearth box is a cast-iron block *n*, and another iron block *o* is at the back. This back stone is perforated for the tuyère *b*, entering the furnace about 2 in. above the surface of the lead in the hearth. *p* is an upper back stone, or cast-iron block; the forestone *m* is small. Brick shaft *c* carries off the fumes; at the back is a pit *d*, or dust chamber, cleaned through door *e*. On the side of the shaft is feed door *k*, for introducing fuel and removal of slag crusts at tuyères. Charge is fed from the front. A



FIGS. 21-24. — Newnam ore hearth

shutter *f* is in place at the front of the hearth, sliding in a frame *r*, it is raised and lowered by counterpoise *s*.

Bituminous coal is used as fuel. After operating from 12 to 15 hr. the hearth becomes too hot and must be cooled for about 5 hr. before work can be resumed.

**The Rossie, or Air-cooled Hearth.**—Figures 16 and 17 show an arrangement of ore hearth in which the sides and back are air cooled. The cast-iron jacket *D* has an air space inside. Blast enters at *E*, passes through *D*, leaves at *F*, and is delivered to tuyère *G*. This cools the walls of the hearth and preheats the blast. The Rossie hearth could be used continuously, but the hot blast caused excessive volatilization,



and this hearth was abandoned until recovery of fume became possible, when it was again brought into use.

*Original American Water-back Ore Hearth.*—Figures 18 and 19 show the water-cooled ore hearth, in which work is continuous, due to the cooling of sides by water, which enters at *i*, and passes out at *k*.

*Modern American Water-back Ore Hearth.*—In this furnace the cast-iron hearth box is supported by short columns in order to air-cool the lead; the upper sides are two water-cooled castings; the inside working length covers about 4 ft.; and two hoods are provided, an inner smaller for carrying off dust and the bulk of fume by means of a suction fan, and an outer for removing the remaining fume by natural draft. Such a furnace is shown in cross-section, in Fig. 20.

*Moffet Ore Hearth.*—Figures 21 to 24 show the combined water- and air-cooled hearth, in double form, *i.e.*, two hearths placed back to back, under one hood. A water box cools the hottest part of the furnace, and upon this rests the air box, consisting of two separate chambers where the heated blast passes down through the water box by means of fourteen 1-in. copper tuyère pipes, seven on a side.

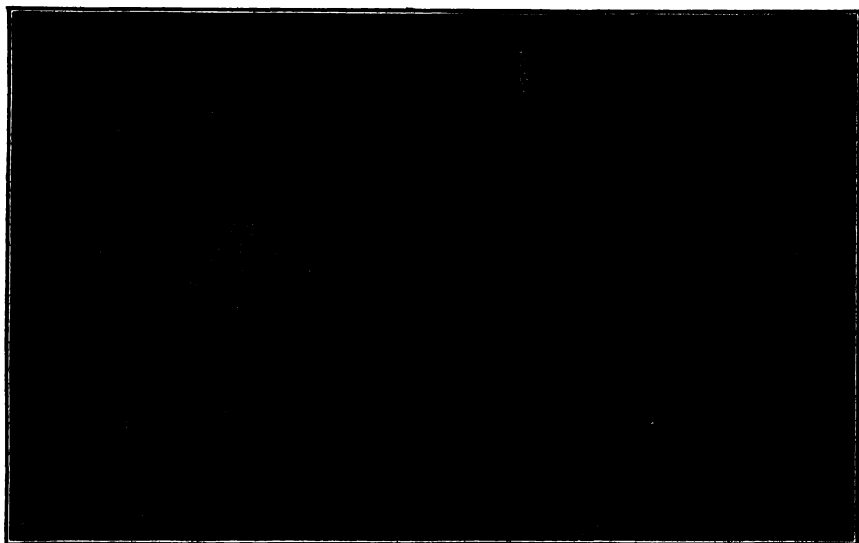


FIG. 38.—Rabbling mechanism—beginning of trip.

These hand hearths have all given way to the Newnam mechanically rabbled furnace, shown in Figs. 26 to 39. Figures 25 and 26 give a front and side elevation; Figs. 27 and 28, horizontal and vertical sections of the lead basin; Figs. 29, 30, and 31, elevations and sections of middle water jacket; Figs. 32, 33, and 34, elevations of right and left end jackets and section of right end jacket; Figs. 35, 36, and 37, details of cast-iron stand supporting the lead basin; and Figs. 38 and 39, perspective views of the furnace with rabbling mechanism at beginning and end of trip.

The basin of the Newnam hearth shown is 8 ft. long, 19.5 in. wide at top, 10 in. at bottom, and 10 in. deep. The furnace has twelve tuyères. Lead discharges from basin through siphon tap, *e* (Fig. 27). The furnace is shown in perspective (Figs. 38 and 39), because the full assembly of detail drawings would be unnecessarily voluminous. The rabbling machine is hung from an overhead traveling carriage.



This carriage starts from its position of rest at one end of the furnace, on the pulling of a lever, and during the trip to the other end the rabble arm is given a motion similar to that of the hand rabble. When the rabble arm is withdrawn from the fire, the carriage moves ahead 4 in. and starts the rabble on the next stroke. When the carriage reaches the opposite end of the furnace (Fig. 39) it is stopped automatically, the rabble arm withdrawn, and the carriage returned to its original position. A 1-h.p. motor is sufficient for driving the axles of the carriage and the rabble arm.

The mode of operating with the Newnam mechanical hearth is the same as that in a hand-worked hearth, except that stirring is done by machinery. The first step in the normal working of an ore hearth is to spread a few shovelful of coal over the fire, and then a thin layer of ore mixed with 0.5 to 1.0 per cent of lime. The fire is left undisturbed for a short time—1 to 1½ min.—during which the charge is more or less oxidized, the flame breaks through, and the ore surface becomes crusted. The rabble arm thrusts over the edge of the basin into the lead and raises and loosens the slightly caked mass. As the mechanical arm rabbles the charge, one man follows it, pushes back the loose charge with a shovel, and drags the gray slag onto the apron

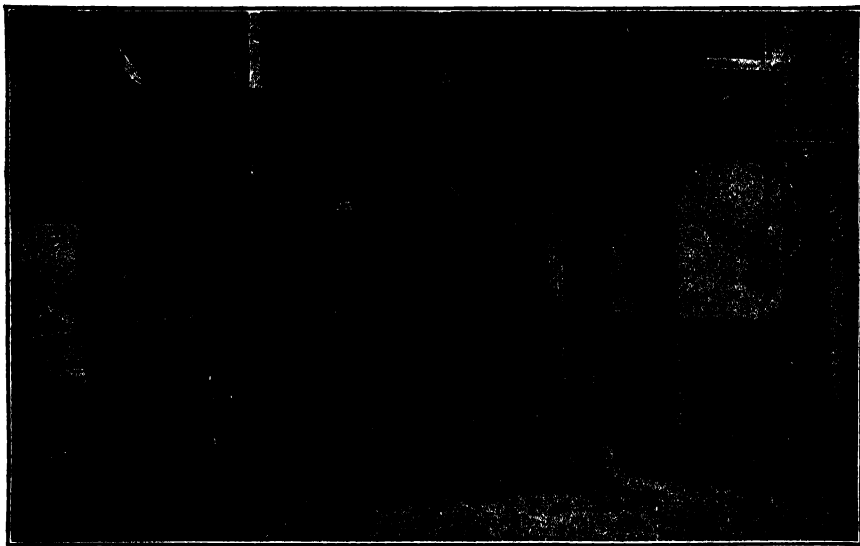


FIG. 39.—Rabbling mechanism—end of trip.

plate. He is followed by a second man (charger), who transfers the gray slag to the water box, spreads a thin layer of ore onto the charge, and adds coke breeze as needed. By the time the trip to the end of the hearth has been covered, the ore first charged at the other end is ready to be rabbled.

The charge is made up of either galena alone, or galena mixed with sintered bag-house fume. Slaked lime was formerly used as a flux; with the substitution of coke breeze for bituminous coal, the greater heat generated has permitted the use of limestone. Fuel used ranges from 3 to 8 per cent of the ore mixture.

From the ore hearth the lead is collected in a pot, in which it is drossed. It is cleaned by liquating and poling, and is then cast into market bars, unless it is to be desilverized in the refinery. The yield in pig lead and the elimination of sulphur are greater in the Newnam than in the hand hearth, the work easier and more healthful, and the cost much less.

Data from leading ore-hearth plants have been assembled (by Hofman) as follows:

EXAMPLES OF SMELTING IN THE ORE HEARTH

Name	Date	Furnace				Products				Materials					Ref- er- ence				
		Front to back	Width	Depth	Sides, kind	Tuyères		Ore in 24 hr., lb.	Lead in 24 hr., lb.	Gray slag in 24 hr., lb.	Per cent lead direct from ore	Men in 24 hr	Bitu- minous coal, lb.	Coke, lb.		Peat bu.	Char- coal, bu.	Wood	Lime bu.
						No.	Diem.												
Rosie Works, N. Y. . . . . Keld Head Mining Co., Eng- land . . . . .	1842	24"	24"	12"	Air-jacket	1	2"	9,988	7,389		73.88	4			*		34		(a)
Leadhill & Warlock, Scotland	1870	23"	21"	12"	Cast-iron	1	3"	10,752	5,064	602	74.44	6	374		12				(b)
Wardale, England . . . . .	1895	22"	30"	6"	Cast-iron	1	3"	...	6,720		61.00	6	500		*				(c)
Waulokhead, Scotland . . . .	1903	21"	27"	8-12"	Cast-iron	1		18,000	8,700		60.00	6							(d)
Granby, Mo . . . . .	1912	22"	30"	6"	Cast-iron	1		...	2,240		60.00	6	560						(e)
Hopewell, Mo . . . . .	1877	22½"	24"	11"	Water-jacket	3		9,000	7,500		83.90	6				27 6		2 5	(f)
Lone Elm, Mo . . . . .	1877	...	29"	12"	Water-jacket	1	1"	6,000	1,464	.....	73.20	6				20 0?			(g)
	1889	22"	48"	10"	Water- and air-jacket	7	1"	27,000	12,032	5,247	45.00	6	2,160					5.40	(h)
Granby, Mo . . . . .	1908	15"	4'	10"	Water-jacket	4		14,000*	...	2,000	75.00	4	*					*	(i)
Galeana, Kans . . . . .	1909	.....	5'	...	Air-jacket	10		21,000			50.00	4	*						(j)
Granby, Mo . . . . .	1911	.....	5'	...	Air-jacket	10					65.00	6	*						(k)
Webb City, Mo . . . . .	1911	18"	5'	7"	Air-jacket	10		14,000*			65.00	6	*					6	(l)
Federal, Ill. . . . .	1914	18½"	4'	10"	Water-jacket	8	1"	22,500	7,200		60.00	6		1,800					(m)
Collinsville, Ill . . . . .	1914	15½"	4'	10"	Water-jacket	8	1"	21,000	6,200		55.00	6		1,680					(n)
Collinsville, Ill <sup>oo</sup> . . . . .	1923	19.5"	8'	10"	Water-jacket	16	1"	52,000	24,400	9,000	67.00	6		2,600					(o)
Joplin, Mo . . . . .	1916	20"	5'5"	10"	Air-jacket	16	1"	28,000	12,600	4,200	60.00	6	1,200						(p)
Galeta, Ont <sup>oo</sup> . . . . .	1917	19.5"	8'	10"	Water-jacket	16	1"	56,000	33,000	8,000	75.13	6		2,000				1,000	(q)

\* 19 tons concentrate, 7 tons by-products.

\* = used \* = works 12 hr. only \* = Newmann mechanical ore hearth.

(a) *Am J Sc. & Arts*, 1942, xlii, 169; (b) Percy, "Lead," 278-283; (c) Sexton, *Eng. Min. J.*, 1905, lxxv, 175; (d) Middleton, *Eng. Min. J.*, 1905, lxxv, 10; (e) Correspondent, *Can. Min. J.*, 1912, xxxviii, 678; (f) Williams, "Industrial Report," p. 63; (g) *Ibid.*, p. 65; (h) Dewey, *Tr. A. I. M. E.*, 1889-90, xxviii, p. 674; (i) Perkins, *Eng. Min. J.*, 1907, xxxv, 388; Buskett, *Min. Eng. World*, 1908, xxx, 917; (j) Brinsmade, *op. cit.*, 1909, xxxi, 1029; Pulster, *op. cit.*, 1914, xl, 450, 501; (k) Brown, *Tr. A. I. M. E.*, 1911, xlii, 402; Pulster, *Min. Eng. World*, 1914, xl, 450, 501; (l) Rubi, *Min. Eng. World*, 1910, xxxviii, 1047; Wittich, *Mines & Minerals*, 1911, xxxi, 706; (m) Pulster, *Min. Eng. World*, 1913, xxxix, 375; 1914, xl, 450, 501; (n) Pulster, *op. cit.*, 1913, xxxix, 631; 1914, xl, 450, 501; (o) Newman, *Tr. A. I. M. E.*, 1916, lxxv, 466; (p) Brinsmade, *Min. Eng. World*, 1909, xxxi, 1029; (q) Newman, 1924, correspondence.

**Zinc-lead Sulphide Treatment by F. L. Bartlett Process.**—There has been, during recent years, at Cañon City, and Florence, Colo., a unique semismelting procedure which joins the metallurgy of zinc and lead, but which is difficult to classify as either a blast-furnace, reverberatory, or hearth method. It has points in common with the hearth treatment of lead ores, with the collection of silver-bearing fumes by bag-house filtering, and with other points of lead smelting, although it resorts to matting rather than lead smelting for the extraction of precious metals.

The ores treated are a mixture of silver- and gold-bearing sulphides of zinc, lead, copper, and iron, averaging, in the early days of the work at Florence, Colo., Zn, 20; Pb, 5; Cu, 1; S, 20 to 25 per cent; with Ag, 6 to 8 oz. per ton; and some Au. A low-shaft, water-jacketed blast furnace, 42 by 156 in. at tuyères, with a smelting column of 5 ft., high percentage of coke, was run with a hot top in order to volatilize as much metal as possible, the action being oxidizing rather than reducing. Furnace campaigns lasted 3 to 5 weeks. The slag carried  $\text{SiO}_2$ , 38;  $\text{CaO}$ , 22 to 25;  $\text{ZnO}$ , 7 per cent; the balance being mainly  $\text{FeO}$ ; it ran low in Pb; contained about 0.2 per cent Cu; and was free of Ag. Matte fall was about 5 per cent. The fume ( $\text{PbSO}_4$ ,  $\text{ZnSO}_4$ , and  $\text{ZnO}$ ) contained all the Pb and Zn, and was caught in a bag house and shipped to Keokuk, Iowa, for electro-deposition of zinc after leaching with  $\text{H}_2\text{SO}_4$ . The insoluble  $\text{PbSO}_4$  residue was smelted for lead bullion.

The heavy percentage of fuel required, cost of labor, and the continuous difficulties of furnace manipulation caused, finally, a change from blast-furnace to reverberatory smelting. The ore for reverberatory treatment was rough roasted in a Wedge kiln, and smelted in a coal-dust-fired reverberatory for matte, slag, and fume. The lead-zinc fume, caught in a bag house, has been reburned on Wetherill grates to produce a low-grade leaded zinc oxide. The fume recovered in the first bag house is impure, and of dark color, and it must be reburnt on the Wetherill grates to purify it into a second bag-house product of first-grade market quality.

This operation has occupied an interesting and unique place in zinc-lead metallurgy for many years, but it has, for one reason and another, never been a permanently profitable procedure. Experiments have recently been under way with chloride-volatilizing methods designed to eliminate the lead from the ore charge, so that a lead-free or low-lead zinc oxide might be obtained. The nature of the complex ores available in the district has been such that the leaded zinc oxide produced has been in the 2% class, a grade that is the least profitable of the leaded zinc-pigment series.

## DESILVERIZATION AND REFINING OF LEAD BULLION

**General.**—The lead obtained from the ores of certain non-argentiferous districts—notably Missouri, Wisconsin, and a part of that from Spain and Germany—is comparatively free from silver as well as from base metals, and can therefore, be used in manufacture practically as it leaves the smelting furnace, after a simple “poling” or blowing with steam, followed by drossing. All the lead produced in blast furnaces from complex ores, however, contains at least enough silver to pay for extraction, and impurities which must be removed from the lead before it is fit for the market.

A desilverizing (refining) plant has for its task not only the separation of silver and the other precious metals (Au, Pt, Pd, and Te) from lead, but also the removal of the impurities Cu, Sn, Bi, As, Sb, S, Fe, Ni, and Co, and the consequent concentration of a bullion carrying 95 to 98 per cent lead to a refined lead of not less than 99.9 per cent lead. These impurities themselves must also be worked up into salable products.

The standard methods of desilverizing lead bullion are four; cupellation, Pattinson process, Parkes process, and Betts electrolytic process. Cupellation has ceased to exist as an independent process, but follows the processes of Pattinson and Parkes as an auxiliary. It can be adopted alone, however, in spite of its high losses and labor cost, for the treatment of rich lead in inaccessible districts where silver is the valuable metal sought. Up to the introduction of the Pattinson process, all argentiferous lead was cupeled; but costs and metal losses are so high that a limit is soon reached where the separation of silver by cupellation is not economical. This limit is at about 30 to 40 oz. silver to the ton of lead. Below this grade, the silver recovered will hardly pay for the labor, fuel, and material used, the loss in metal, and the inferior grade of lead obtained from the subsequent reduction of the litharge produced in cupellation. It becomes necessary, then, to concentrate the silver into a smaller amount of lead before cupeling, and this is done by the Pattinson and the Parkes processes.

The process of desilverization must be preceded by a process of oxidation to remove the foreign-metal impurities in the furnace lead, this being called "softening," in America, and "improving" in England. Almost all the impurities in the furnace-lead interfere, to a greater or less degree, with desilverization by either Pattinson or Parkes processes. Generally speaking, the Parkes process requires a purer bullion than the Pattinson.

Arsenic and antimony are the most troublesome impurities, interfering greatly, even when present in very small quantities. Next in order among harmful impurities come Sn, Zn, S, Fe, Ni, and Co. Fortunately, all of these have a greater affinity for oxygen than lead, and can, therefore, be removed by simple oxidation at a low red heat and a skimming of the molten bath.

Copper has less affinity for oxygen than the other impurities mentioned and is only partially removed by oxidation. It does form, however, an alloy with part of the lead itself, which is less fusible than pure lead, and resort is had to this characteristic to accomplish its removal.

Bismuth cannot be practically separated from lead by oxidation, as it has less affinity for oxygen than has lead itself. It does not interfere with desilverization, but it stays with the refined lead in the Parkes process, and renders this lead, when present, "non-corroding," *i.e.*, unfit for production of white-lead paint. Refined lead containing over 0.05 per cent bismuth is not classed as corroding lead, because Bi gives white lead a grayish color. The presence of any considerable amount of bismuth in lead bullion, therefore, determines the method of refining to be followed. There are two ways of removing it from lead; one is the Pattinson process, which, while not giving a perfect separation, is sufficient for practical purposes; the other, the Betts electrolytic process, is completely effective, as bismuth is not deposited on the cathode, but remains in the anode mud.

The many advantages that the Parkes process has over that of Pattinson have made it the preferred and most generally used desilvering process in American practice. The Parkes method is the cheaper (20 to 50 per cent); produces market lead lower in silver content (4 to 6 dwt. as against 9 to 15 dwt. by Pattinson); completely recovers even traces of gold; produces a lead for cupellation with 2,000 to 5,000 oz. silver per ton as against 500 to 650 oz. by Pattinson; and shows much lower loss of lead and silver.

A combination of Parkes and Pattinson processes is sometimes used when bullion is high in bismuth, the desilverizing being performed by means of the Parkes and the bismuth content of the desilverized lead being lowered by Pattinsonizing to 0.05 per cent, the dividing line between corroding and non-corroding lead.

**Softening and Refining.**—The softening or "improving" of lead bullion as a preliminary to desilvering by either the Parkes or the Pattinson process is essential. It is partially accomplished in the dressing plants of lead blast-furnace smelteries

which, having no refinery on the premises, must ship their base bullion to distant points for desilvering. But the major part of the softening operation is accomplished in any case at the refinery proper. In the Parkes process, it has been shown by Kirchhoff<sup>1</sup> that a decided saving in zinc consumption exists between the respective treatments of bullion which had been softened and bullion which had not been softened. For an unsoftened bullion containing 4.5 per cent foreign metals—such as Cu, As, Sb, Bi, and Zn—2.87 per cent zinc was required to desilverize the lead, whereas 1.75 per cent zinc sufficed if softening had preceded desilverization; the relative recoveries of market lead were 43 and 72 per cent of the bullion charged.

As the refining of the desilverized lead is conducted along the same lines and in apparatus of the same nature as the softening operation, refining and softening will be discussed together, thus bringing refining somewhat in advance of its place in the cycle of the operations.

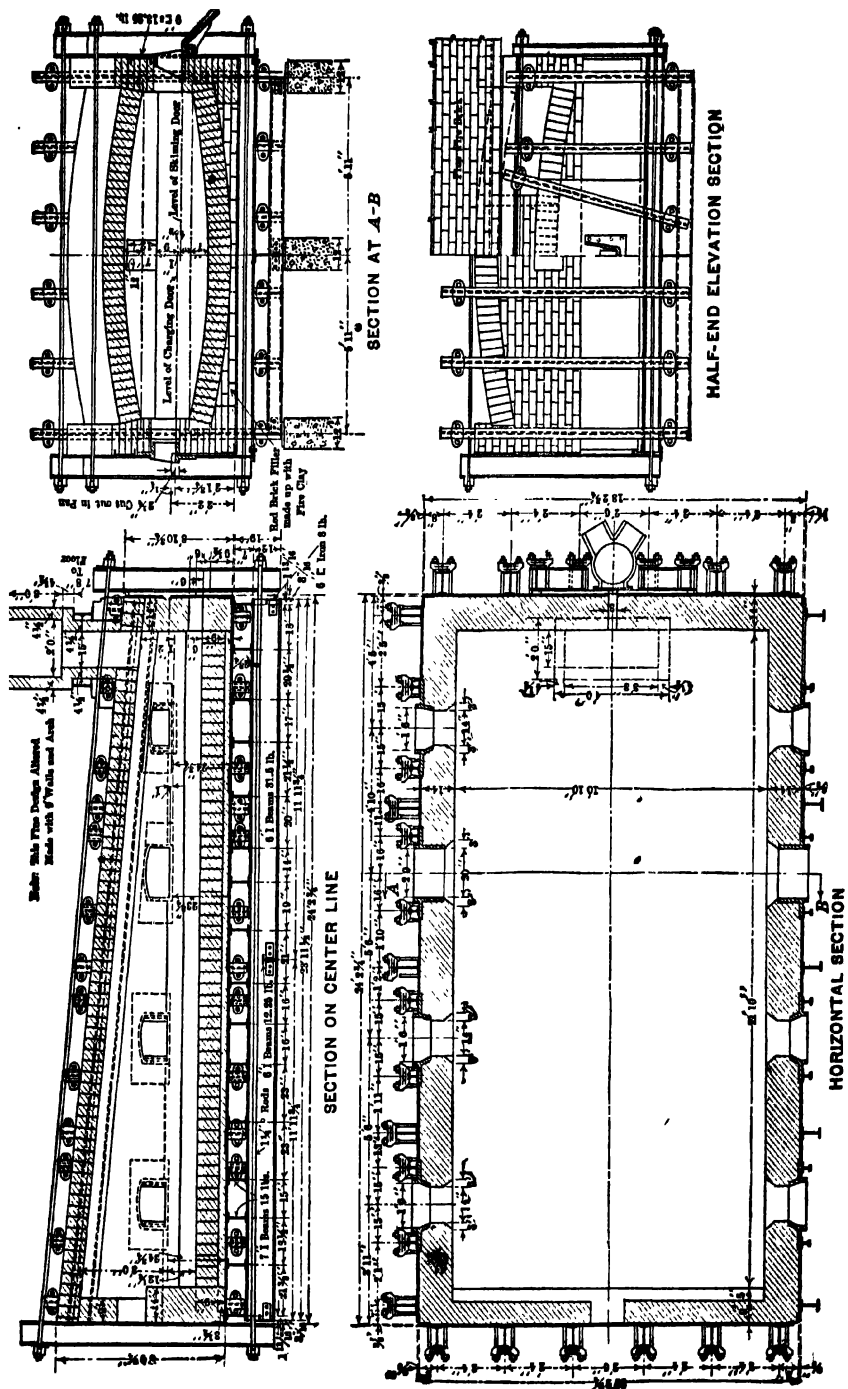
Both the softening and the refining of lead may take place in cast-iron or steel kettles, or in reverberatory furnaces. If free from antimony and arsenic, and containing only small proportions of copper, bullion can be softened in kettles, but reverberatories are more commonly used, since they are adapted to the treatment of more impure lead containing large quantities of copper, arsenic, and antimony. The great drawback of kettle refining is the wear and tear of the kettles, which, beside cracking, are corroded away at the surface of the metallic bath by lead antimoniate. The kettle method has given way to the more economical reverberatory furnace at almost every important point, apart from a few German works.

Softening has for its object the removal from the blast-furnace base bullion, of the impurities that interfere with desilverization, mainly, Cu, Sn, As, Sb, S. The operation consists of two stages, liquation (or drossing), and oxidation. By liquation, metals held in solution by the furnace lead are separated from the lead by slow melting at a low temperature. By oxidation, which later occurs when the temperature is raised to a bright red with access of air, metals alloyed with the lead are converted into oxides which are to some extent volatilized, but which mostly combine with the PbO formed at the same time and are slagged off.

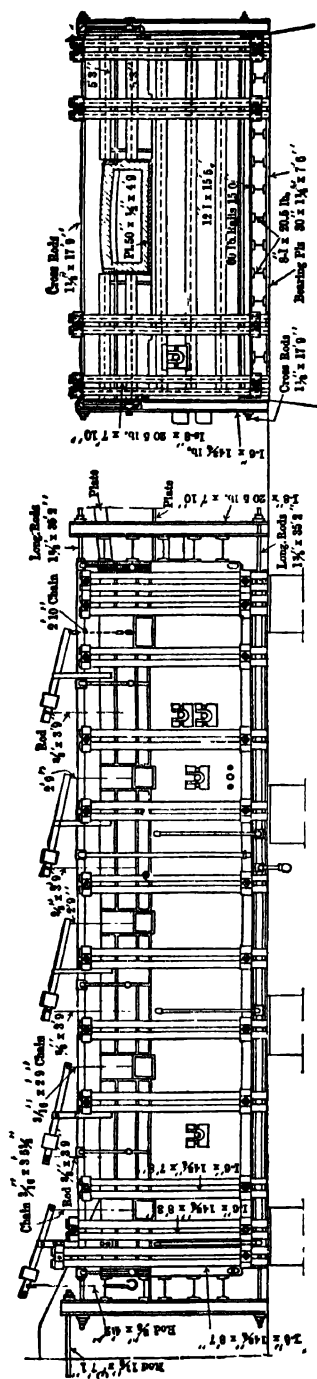
In the first step, the bullion is slowly melted at 370 to 380°C., and there rises to the surface a dross consisting principally of Cu, S, As, Pb. In the second step, when the temperature has been raised to a good red heat the three principal impurities alloyed with the lead are oxidized in the order: first Sn, then As, and lastly Sb. The surface of the bullion becomes coated with dark-yellow, powdery "tin skimming," mainly antimoniate and stannate of lead and antimoniate of tin. As soon as the tin skimming has been removed, the lead begins to give off fumes of arsenic and antimony, and arseniate and antimoniate of lead begin to form. These are drawn off together as an "antimony skimming," after the furnace has been cooled sufficiently to cause the skimming to solidify. The last traces of antimony come out with difficulty, and to hasten the process rich litharge from the finishing cupels can be stirred into the bath efficaciously.

Jets of steam have sometimes been introduced through perforated pipes, to stir the bullion and to hasten the oxidation, but the wave motion set up on the surface of the bath has the bad effect of corroding the walls at the lead line. Before the antimony has been removed, a sample of the bullion will "work," i.e., it will show small, greasy, particles of revolving black skimming on the surface of the lead. As the softening approaches and reaches the end point, these globules disappear, and a thin yellow litharge forms.

<sup>1</sup> *Met. Rev.* (1877-1878) I, 224.

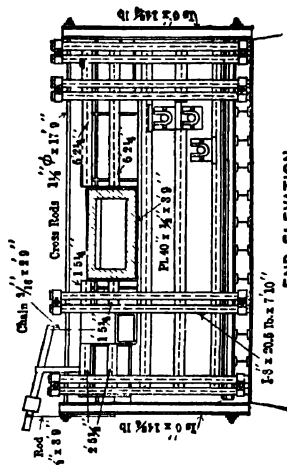
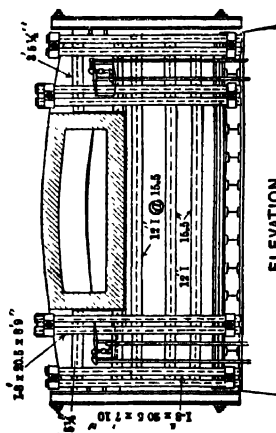


**FIGS. 40-43.—60-ton softening furnace.**

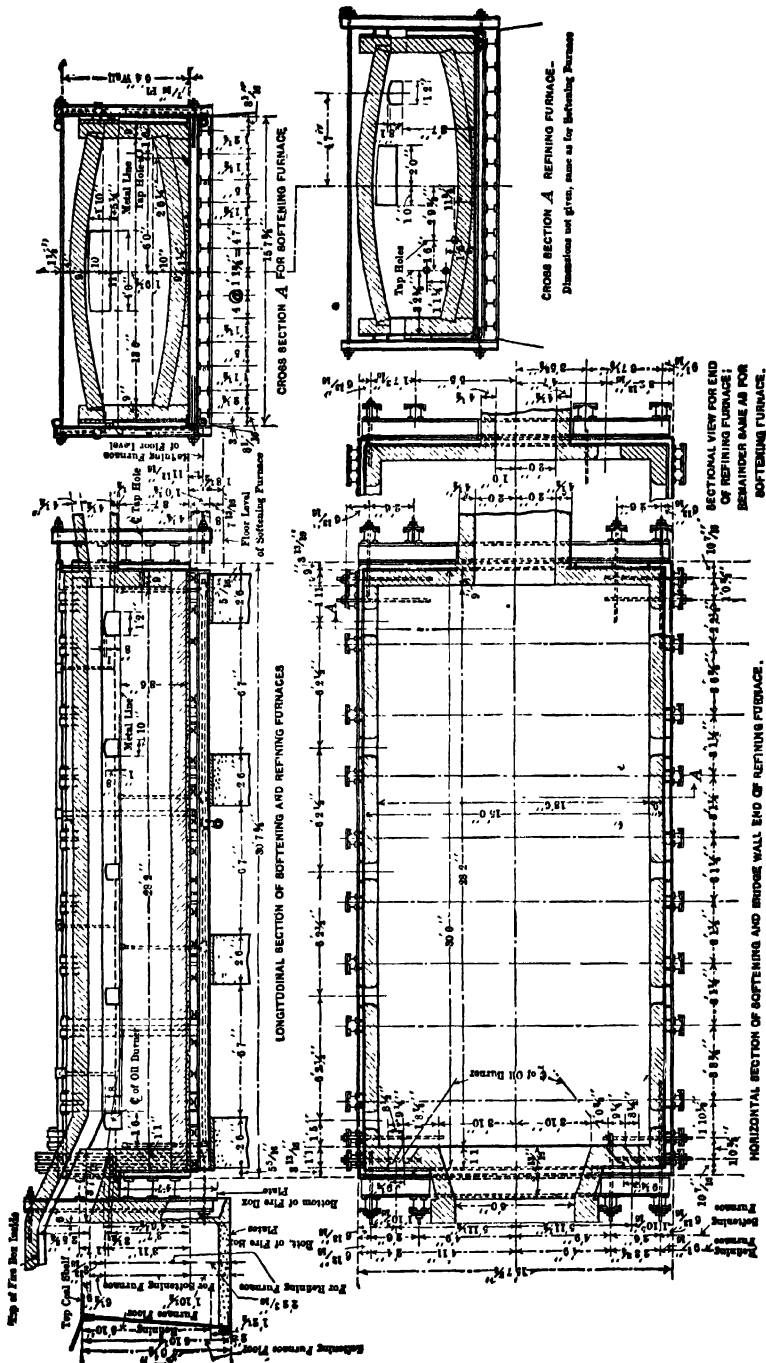


SIDE ELEVATION

Note: Eye Holes and Spurts are omitted on opp. side of Refining Furnace and on both sides of Softening Furnace.

END ELEVATION  
SOFTENING FURNACEEND ELEVATION  
REFINING FURNACEELEVATION  
BRIDGE WALL END

Figs. 44-47.—300-ton softening and refining furnace.



Figs. 48-51.—300-ton softening and refining furnace.



The furnaces used for both softening and refining, in American practice, are shown in Figs. 40 to 43 (60-ton softening furnace, Selby Works, Cal.) and Figs. 44 to 51 (300-ton softening and refining furnace, International Lead Refinery, Chicago).

The general construction of the reverberatory used for refining is the same as that for softening. It was formerly customary to build the refining furnace smaller than the softening, in order that it might correspond to the smaller amount of final lead to be treated, but of late it has been more common to give both furnaces the same overall dimensions, making the hearth of the refining unit slightly shallower.

It is common practice carefully to cross base bullion at the blast furnace itself, in a kettle, before casting it into bars for transfer to the refinery. When this has been done, and the base bullion contains about 1 per cent of impurity, the mode of operating the softening furnace can be regulated so that the entire time required for charging, softening, and tapping does not exceed 24 hr. With bullion overly high in antimony, it is sometimes not possible to do the work in 24 hr.

The fuel consumed in softening ranges from 2 to 12 per cent, and averages 5 per cent, of soft coal, by weight, of the market lead produced. Fuel oil is, in some localities, considerably more economical. After the softening operation, the bullion goes to whichever desilvering process is provided—Parkes or Pattinson—and the desilverized lead must then pass on to its refining treatment, for the removal of the 0.6 to 0.7 per cent zinc which it contains (from the Parkes process) as well as the small amounts of arsenic and antimony which may not have been entirely removed during the softening or that were introduced with the zinc used in desilverizing (usually Prime Western spelter with 1.5 per cent lead and 0.06 per cent iron). If the desilvering has been by means of the Pattinson process, refining is sometimes necessary to remove the arsenic and antimony retained in the crystallized poor lead. It is, in general, more feasible to conduct the refining operation in steel or iron kettles than it is to soften in this form of apparatus. Whenever the work in the softening furnace has been very thoroughly done, the lead, after desilverization, is practically free from antimony, but contains zinc. If the Parkes process has been used, it is antimony, and not zinc which brings about the greatest destruction of kettles.

The mode of operating the refining furnace is similar to that in the softening furnace, except that a higher temperature is necessary. The last traces of antimony, when the bullion has not been thoroughly softened previously, are difficult to remove in refining, and sometimes three heatings and skimmings are required, taking about 12 hr. total time, before all zinc and antimony are oxidized and removed. A lead containing 0.6 per cent zinc and 0.3 per cent antimony will yield as much as 5 per cent of skimmings containing about 90 per cent lead.

In order to hasten the operation, steam is used; in addition to the mechanical effect of stirring it acts chemically, being decomposed by the zinc at 900 to 1000°C. It is true that the wear and tear on refining furnaces from the use of steam is even heavier than on softening furnaces, due to the higher temperature that prevails, but its advantages warrant its use.

The time required for refining, without the use of steam, ranges from 10 to 15 hr. with five or six steam jets in play.

**Harris Process.**—A new and radically different method of softening, is the Harris process, now in use at refining plants in Europe, a secondary-metal plant in New Jersey, and under construction at several other points in Europe and America, and one in North Africa. This process is also applicable to the refining, or dezincing of desilverized lead. It thus both precedes and follows the standard desilverizing operation by either the Parkes or the Pattinson process.

This process is designed to accomplish the removal of such impurities as arsenic, antimony, and tin from base bullion or any other metallic-lead material, and the removal of the zinc from desilverized lead.

This is done by bringing about an intimate contact between the metal, at a temperature not greatly in excess of its melting point, and molten caustic alkali (soda) and alkali chloride. A clean separation takes place, thereby, of the lead from its impurities—arsenic, antimony, tin and zinc, which are quantitatively collected in the form of their oxides or oxysalts suspended in, or otherwise associated with, the chemicals. The latter are treated by a wet process for the recovery of the contained reagent and of the oxides and oxysalts derived from the impurities removed from the lead.

The circuit of the wet process is closed and complete, rendering a recuperation of 95 per cent of the free chemicals possible, which, in turn, are used again in the process for the refining of lead. The impurities are also completely and separately recovered and are free from either lead or other impurities. Arsenic and zinc (the latter from desilverized lead) are directly obtained in salable form, the former as calcium arsenate, the latter as zinc oxide, while the recovered antimony and tin compounds can readily be reduced to metal.

The essential feature of the Harris process, therefore, is that, by its application to the refining of lead and its alloys, a clean separation of the constituents is made possible, each of them being recovered completely and in marketable form. The operation is all performed in, and above, the regular refinery kettles, without furnaces—the pumping apparatus and chemical treatment tank being a portable unit which is swung onto the top of the kettle, and removed when purification is complete.

Another recent innovation in softening procedure is the Colcord process, which removes copper and arsenic from the bullion as the first operation in refining. Sulphur is stirred into the metal with a Howard stirrer, at a temperature (about 600 to 650°F.) sufficient to cause the sulphur to unite with the copper. Temperature is then raised (to about 700°F.) until the copper sulphide readily separates as a dross. The next step in the process is to add caustic soda to the metal, raise the temperature to between 900 and 1000°F., and thoroughly stir the caustic soda into the metal, using a Howard stirrer, air jets, or other mechanical means. The arsenic content of the metal can be reduced to any desired quantity by fractional additions of caustic. The sodium arsenate in the caustic skim is suitable for manufacture of insecticides by leaching with water. The leached residue, containing lead and a little antimony, can be readily treated.

**Molding of Refined Lead.**—The refined lead was formerly ladled by hand from the kettle into molds placed in front of it. This operation is now performed by mechanical devices. The refined lead is run into molds either directly from the reverberatory or kettle in which the zinc and antimony had been removed from the desilverized lead, or, as is more common practice with plants having large units, the refined lead is tapped into a storage reverberatory furnace or a market kettle, from which it is run into molds. The storage reverberatory is of the same capacity as the refining furnace, and its general construction similar, except that it is not water jacketed.

The lead is usually run from the furnace through a pipe, provided with regulating cock, into a cast-iron trough which tilts on trunnions. The side of the trough has a number of 1-in. spouts, through which the lead flows into the molds when the trough is tilted by means of an air lift. The molds in the older forms of casting machines—similar to the Walker machine for copper casting—are carried by an endless link-chain conveyor which travels in a horizontal direction in front of the trough. The conveyor travels up an incline beyond the trough, whereupon automatic trimming and

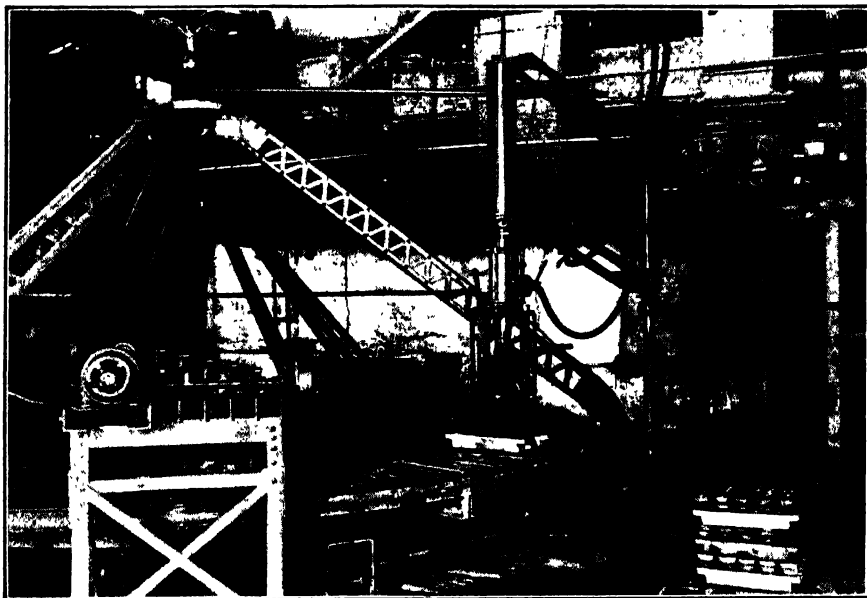


FIG. 52.—Five pigs just being lifted by Newnam pig-pulling and stacking machine.

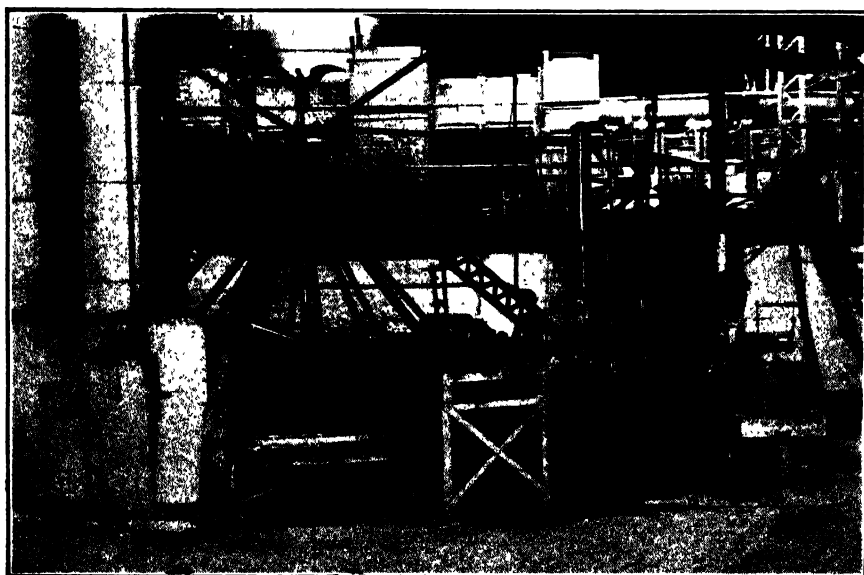


FIG. 53.—Casting wheel, cooling head and lead truck.

stamping of the lot number is accomplished. Bars are cooled, during travel, by water sprays from below. Arriving at the top of the incline, they drop off, one after another, onto a truck. In molding five or six bars at a time in this way, the trough travels with the conveyor while pouring, and is arranged with mechanism which returns it to its original position at twice the normal speed. The rate of molding by this method is 35 tons per hour.

Another method of molding is by means of the Miller casting machine, a vortical iron wheel with molds and periphery water-jacketed, which handles 12.4 tons lead per hour, with three men.

The latest improvement in the molding and loading of pig lead is the Newnam system, a horizontal-wheel type of machine which handles 40 tons per hour with four men. In this device the pigs are at no time touched by hand. The molds are arranged in sets of five parallel pigs, forming practically a square, and five pigs are poured at a time. As the wheel revolves, the pigs are cooled and pass under an automatic stamping machine. They then encounter a pig-pulling and stacking machine which lifts the pigs out of the molds in sets of five and places them in a stack of thirty-five, weighing approximately 3,200 lb. The stack is picked up by an electric truck, which, after passing over scales, places it in a railroad car. This system is becoming popular (1923) because it takes a minimum amount of space and labor, and can be installed in any plant which has the old-fashioned method of molding from a central kettle by a radial trough through a half circle, which takes six or seven men to do the work.

A typical American and a typical Australian (Parkes process) market lead, of corroding quality, analyze:

	American	Australian
Ag	0 0010	0.0012
Bi	0 0300	
Sn	0 0004	
As	0 0024	
Ni	0 0001	
Fe	0 0027	
Zn	0 0003	0.0010
Mn	0 0008	
Insoluble	0.0040	
Cd	Trace	
Sb	None	0 0060
Co	None	
Cu	None	0 0001
Pb (by difference)	99 9579	99 9917

**The Parkes Process.**—This method of separating silver from base bullion is based on two facts—(1) the greater affinity of silver for zinc than for lead; and (2) the insolubility of zinc-silver alloys in lead which is already saturated with zinc. The process consists, in brief, of stirring 1 to 2 per cent of zinc into a bath of molten lead, heated to above the melting point of zinc (415°C.) and allowing it to cool, when a crust rises to the surface containing nearly all the silver. A repetition of the zinc addition, in smaller quantity, gives another, lower, silver

crust, and leaves a molten lead which is practically free from silver, containing usually not more than 6 dw. per ton.

The zinc crusts, which contain considerable lead beside the zinc and precious metals, are distilled in retorts for the recovery of zinc and to obtain an enriched retort bullion which is cupelled for doré silver, with litharge as a product. A flow sheet of the process is shown, giving this brief outline in greater detail.<sup>1</sup>

In addition to combining with silver, zinc has an affinity for other metals present, notably gold and copper, with both of which it combines before taking up silver. Gold is entirely extracted by the first zincing, and copper enters the zinc crust almost as readily as gold, though not quite so completely. It is found that a gold-copper-zinc

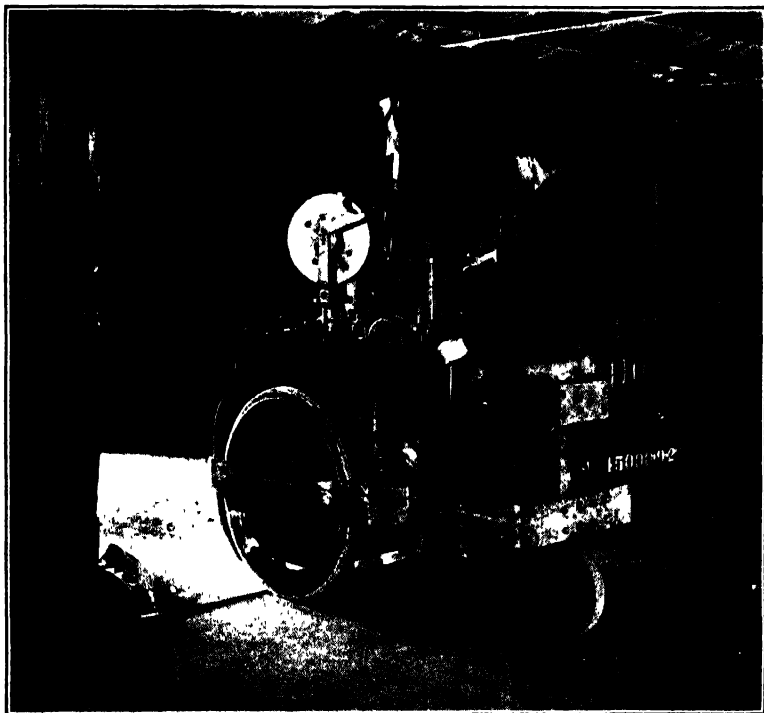


FIG. 54.—Newnam lead truck entering car.

crust is formed, containing all but the minutest trace of the gold present, long before the lead itself begins to take up zinc, the gold-zinc and copper-zinc alloys being apparently almost insoluble in zinc-free lead. It is impossible, in the matter of silver, however, to produce a crust without first saturating the lead with zinc.

Bismuth does not interfere at all with the desilverization, but antimony in amounts as small as 0.1 per cent, as well as arsenic in even smaller proportion, not only retards the rising of the crusts but actually prevents a clean separation from the underlying lead. If the work lead (softened base bullion) contains upwards of 0.1 per cent antimony or 0.05 per cent arsenic, it is difficult to turn out, with only three zincings, market lead of only 6-dwt. silver.

The importance of thorough softening is apparent. Arsenic is, fortunately, much more readily oxidized than antimony, so that it is completely removable by an 8-

<sup>1</sup> HOFMAN, H. O., "Metallurgy of Lead," p. 508, 1918.

or 10-hr. softening, and the critical point becomes one of antimony removal. Copper is readily removed by repeated drossing in the softening operation. If this has not been thoroughly accomplished, an excessive amount of copper-zinc crust is formed in the desilverization before any silver can be extracted. Nickel and cobalt

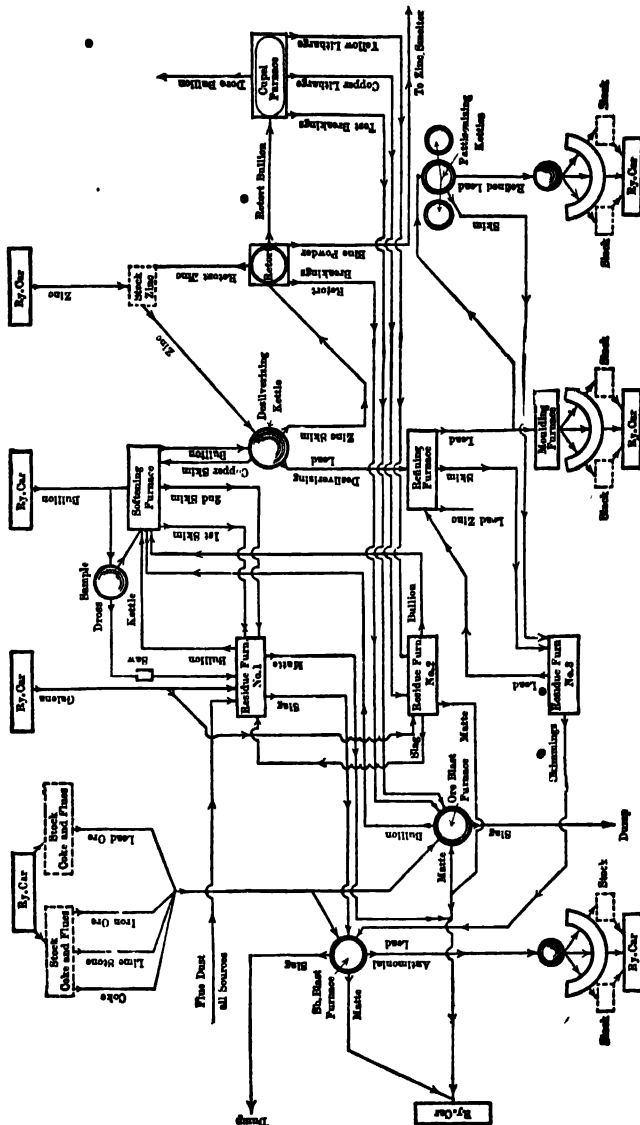


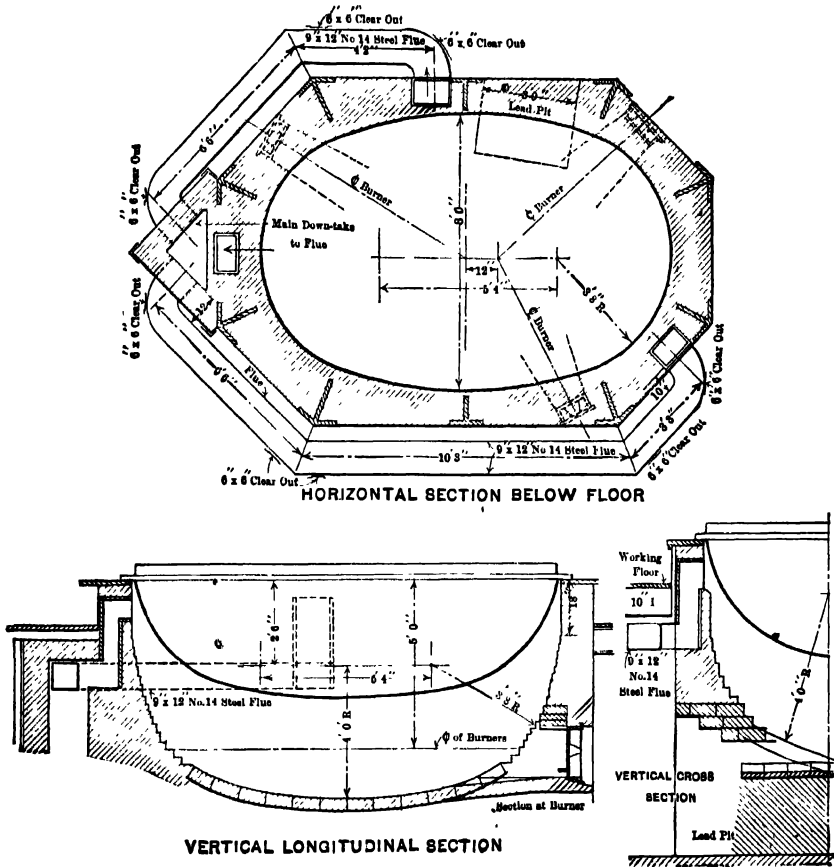
Fig. 55.—Flow sheet of lead smeltery and refinery.

have a tendency to enter the zinc crust like copper, but both these metals are readily removable in the drossing operation.

In ordinary zinc desilverization, there are present, in varying amounts, beside Ag, the metals Au, Cu, Pt, Pd, Te, Bi, As, Sb, Sn, Ni and Co in the base bullion and Cd and Fe in the spelter. Of these, Ag, Au, Cu, Pt and Te readily enter the zinc crust.

The others do so only to a slight degree; they interfere, more or less, however, with the work the zinc has to do.

The quantity of zinc necessary to accomplish desilverization depends, of course, on the purity of the lead and the amount of silver present. If the lead is practically pure, it will hold in solution between 0.6 and 0.8 per cent zinc, at about 400°C. This quantity has to be added to the kettle as a constant, before the lead will give up any of its silver. Thereafter, the quantity of zinc required for combining with silver must be provided on a basis of  $\text{Ag}_2\text{Zn}_3$ . It is found, in practice, that it is not possible

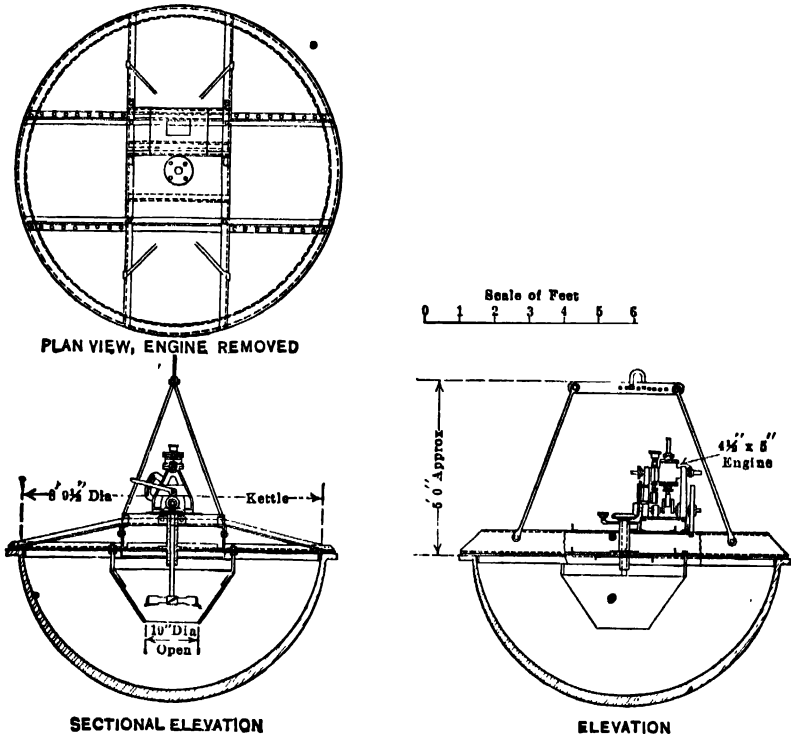


FIGS. 56-58. --Oval desilvering kettle.

to desilverize high-grade lead bullion by a single addition of zinc. If no gold crust is made, it is fairly uniform practice to desilverize by means of two additions of zinc. The aim is to concentrate as much silver (and all the gold) as possible into the first crust, which, assaying over 2,000 oz. of silver per ton, goes to the retorts. In the second zincing, an excess of zinc over that required for the amount of silver present is used; this is necessary if the silver is to be thoroughly removed from the lead. The resulting crust is unsaturated and is used to take the place of part of the fresh zinc needed in the subsequent first zincing. This second crust assays about 10 to 30 oz. of silver per ton.

The gold is taken out with the silver, the doré-silver crust retorted, the retort bullion cupeled, and the doré silver parted either with  $H_2SO_4$ , or electrolytically. The making of a separate gold crust is not economical, or usual, in the United States, as it takes time, and requires separate storing and handling of two classes of products, and because the lead bullion retains small amounts of gold in spite of the greatest care given to the gold-crust operation.

The cast-iron or steel kettles used for desilverization were restricted to 40 tons capacity when the zinc stirring was done by hand. With mechanical stirring (Howard stirrer, Figs. 59 to 61), kettles have increased in size to hold 60 and 100 tons softened bullion. An 80-ton oil-fired oval desilverizing kettle is shown in Figs. 56 to 58.



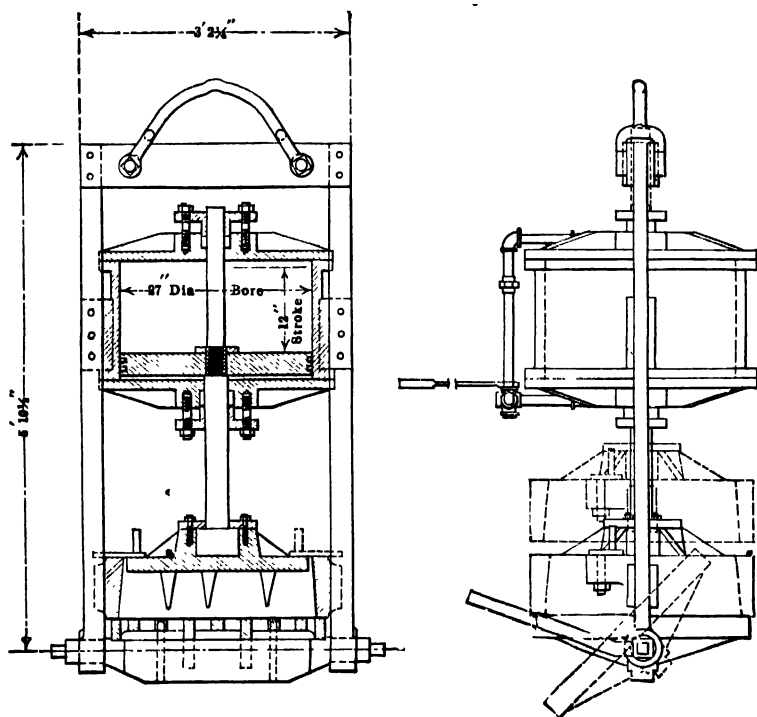
FIGS. 59-61 -- Howard stirrer.

For freeing the zinc crusts from adhering lead, the Howard press has come into general use, replacing the liquating kettles or reverberatory furnaces that were formerly used for the purpose. This press consists of a steel frame suspended from an overhead crane, which carries near the upper end an air or steam cylinder with a 12-in. stroke piston, and at the bottom a heavy perforated tilting plate. The plunger of the piston has projecting teeth on its lower side. This movable portion is held in position by flanges gliding on a vertical member of the frame. When filled with crust, the frame is raised to bring the bottom plate just above the surface of the lead, and the plunger is forced downward to squeeze out, at a pressure of 90 lb. per square inch, the excess lead from the crust, flowing through the perforations back into the kettle. The whole apparatus is then swung to one side, the bottom plate carrying



the pressed crust is lowered and tilted, and the crust dumped. This ingenious device, shown in Figs. 62, 63, has revolutionized the handling of zinc crusts; it also finds use in removing lead from drosses skimmed from lead which has been melted in a kettle.

The desilvering operation proceeds as follows: When the softened base bullion in the kettle has been drossed and brought to about  $482^{\circ}\text{C}.$ , cakes of crust from the preceding second zincing are charged, and sufficient new zinc also added. In some works the floor zinc is charged first into the empty kettle, melted, and then the fresh spelter added; and then, only, the bullion tapped into the kettle from the softening furnace; and the whole stirred for 20 to 30 min. In any case the crust and spelter must be incorporated in the bullion and the zinc brought into intimate contact with the precious metals and copper, by thorough stirring. In some plants a shoveful of sal-



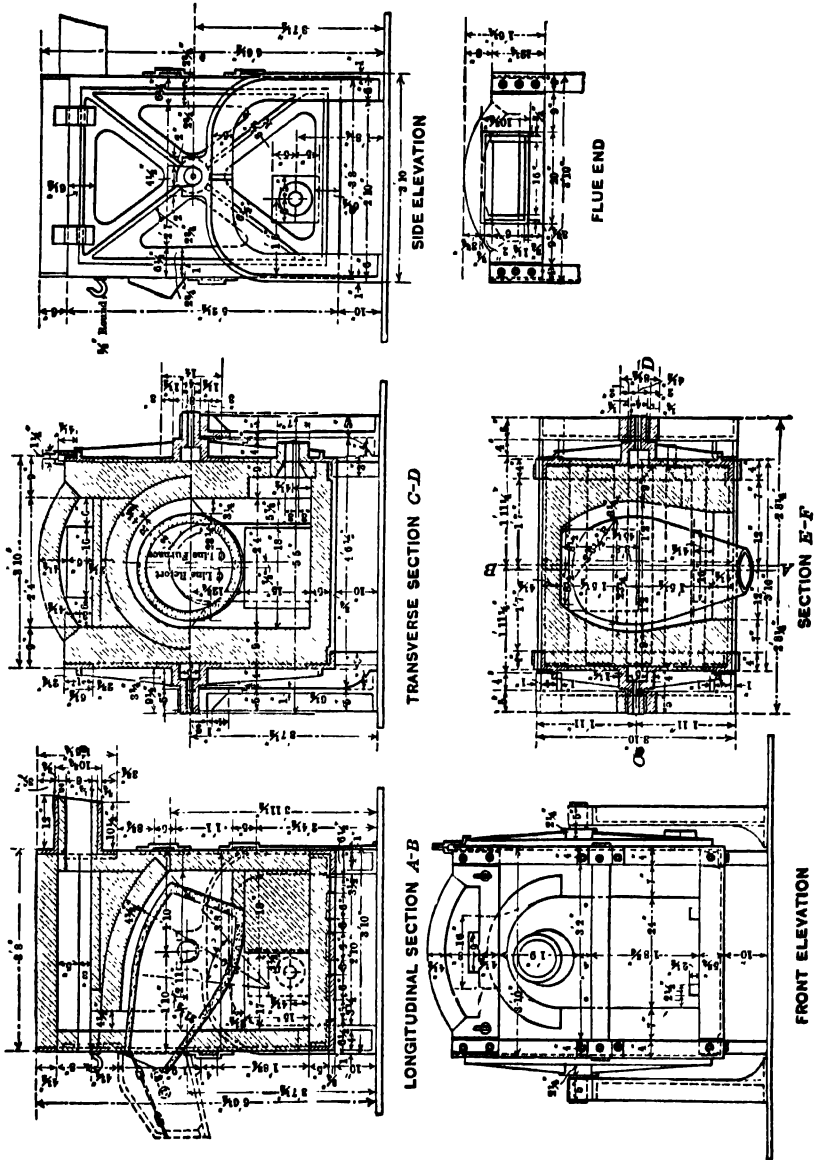
FIGS. 62-63.—Howard press.

ammoniac is thrown into the kettle before stirring—about 1 lb. to 10 tons of lead—for the purpose of keeping the tools clean and counteracting the oxidation of crusts. Hand and steam stirring have given way, generally, to the Howard stirring machine, a vertical shaft with four propeller blades which revolve at 110 r.p.m. in a sheet-iron cone suspended, from rods, into the bullion. The metal within the cone is forced out at the bottom, with constant replenishment at the top. On reversal of the engine the flow of metal is in opposite direction. Air can be almost completely excluded and oxidation of zinc and lead minimized.

After, say, 30 min. stirring, the first crust is taken and pressed hot in the Howard press, in  $1\frac{1}{2}$  to 2 hr. The second addition of zinc is then made and stirred in with the Howard machine. The two zincings usually require, for a 60-ton kettle, about 8 hr. for completion. The first crust is skimmed without lowering the temperature of the

lead appreciably, but in skimming the second crust the temperature is lowered until all the crust, that can be made to, rises to the surface.

The weight of the crust varies with the amounts of silver present. On a 60-ton kettle and 150-oz. bullion, the first crust weighs about 5,200 lb., the partly desilvered



**FIGS. 64-69.—Oil-fired zinc-crust furnace.**

lead assaying 40 to 60 oz. of silver per ton. The second crust will weigh 18,000 to 19,000 lb., the desilvered lead assaying less than 0.2 oz. of silver per ton. Two men in addition to the fireman usually do the work on a kettle. About 2 tons of coal per 8-hr. shift are consumed.

**Treatment of Zinc Crusts.**—Many methods have been tried for working up the zinc crusts: distillation, smelting, cupellation, alkali-chloride fusion, steam oxidation, ammonium carbonate leaching, but only one has survived, the distillation of the zinc from the crust in a coke- or oil-fired retorting furnace. An oil-fired furnace is shown in Figs. 64 to 69. This subject is treated *in extenso* on pp. 925 and 928.

**Treatment of Intermediary Products.**—Refineries tend to accumulate a large assortment of by-products which must be worked up into marketable products currently with the major operations, or else the plant becomes badly clogged with odds and ends. These intermediary products are of the following nature and disposal:

1. *Softening-furnace Dross and Skimming.*—The drosses from the softening furnace are usually not of great amount, since the lead bullion has been largely freed from dross at the smelter. The drosses from the softener are, therefore, not kept separate from the skimming. Where the dross is treated by itself, the procedure is a simple liquation in a small reverberatory. The furnace is charged and heated until the lead that liquates out of the dross forms a bath, on which the dry dross floats. When sufficient dry dross has accumulated, it is pulled out through the furnace door. The temperature is always low, so that no dross is again melted into the lead. The dry dross recovered is smelted in the blast furnace; the lead goes to the softening furnace.

The treatment of antimony skimming is an important process; it is from this by-product that hard lead (antimonial lead) is obtained. This skimming is smelted in a reverberatory furnace with the addition of high-grade galena or of stibnite. The metallic lead reduced from the skimming by these sulphides and fine coal spread over the charge, collects on the bottom of the hearth, and contains all the precious metal of the skimming. This lead, carrying about 1.5 to 4 per cent antimony, goes to the softening furnace. The matte produced (carrying Cu, Pb, Sb, and S) is treated by concentration smelting. The liquated or refined skimming, now carrying 15 to 20 per cent antimony, some As and Cu, and about 1 oz. of Ag per ton, goes to a special blast furnace reserved for producing hard lead, in which it is smelted with approximately 100 per cent slag and 11 per cent coke, with a slag not overly ferruginous, so that speiss will not be formed in great amount. In order to keep down the loss of antimony by volatilization, galena is added to the charge, its sulphur acting as a reducing agent. Only enough is added so that no matte is formed, say from 13 to 28 per cent of the weight of the skimming. This addition of galena reduces the tenor of antimony in the resulting hard lead, but the latter is of good marketable grade if it carries 15 to 18 per cent antimony. Antimony ore—either sulphide or oxide—is sometimes also added to the blast-furnace charge. The hard lead finally obtained is usually poled in a kettle, or liquated in a reverberatory furnace, in order to remove, by drossing, the copper that had remained in the skimming from the softener and been reduced into the hard lead. The dross from liquating hard lead sometimes shows a copper content as high as 40 per cent, usually about 10 per cent.

2. *Kettle Dross.*—Consisting usually of lead oxides mixed with metallic lead, is returned to the softening furnace.

3. *Refining Skimmings and Polings.*—These carry considerable zinc (8 to 10 per cent), some antimony, and about 75 per cent lead. These refining skimmings are sometimes charged into the softening furnace, after its dross has been removed, in order to assist in the oxidation of arsenic and antimony. But they are best treated in a special reverberatory, or in the same reverberatory that is used for liquating

**hard lead.** If the latter reverberatory be utilized the lead resulting from the refining skimming will be high in copper, but if a separate reverberatory be used, corroding lead can be produced. The procedure in treating these refining skimmings is to mix the skimming with about 10 per cent of fine coal, and heat until no more lead flows from the charge. The residue contains Pb, Zn, Sb, As, and coal ashes, and is added to the smelting charge of liquated softener skimming for the hard lead blast furnace.

4. *Rich Lead*, high in silver, goes to the cupeling furnace.

5. *Metallic zinc*, containing a few ounces of silver, is used in desilvering, forming part of the zinc additions.

6. *Retort Dross*.—This is high in silver and is disposed of in one of two ways. In large refineries, where the retort bullion with its floating dross is poured into an operating cupeling furnace from the pot which has received it from the retort, the silver is, of course, recovered with the silver of the rich lead. In smaller plants, this retort dross is worked off, a little at a time, in the regular cupeling, or in some cases it is charged back into the retort itself. Accumulations of this dross are sometimes worked off on the bath of lead, low in silver, with which a new test, *i.e.*, removable bone-ash hearth of the cupeling furnace, is usually charged. Sometimes the retort dross is added to the softening furnace after the latter's dross has been removed. This permits the silver of the retort dross to be taken up by the lead, and the impurities oxidized into the skimmings.

7. *Blue Powder*.—This is a mixture of metallic zinc and zinc oxide, with about 5 oz. of silver per ton, and is an awkward product for disposal, as it yields only some 50 per cent of its zinc on distillation by itself. At some plants it is returned to the retort with the next charge of zinc crust; at other plants it is added with the first zinc to the desilvering kettle, where it serves to saturate the lead with zinc, and to assist in the removal of gold and copper. It is, at still other plants, disposed of by sale to outside zinc works, or converted into lithopone.

8. *Litharge*.—This is reduced in a reverberatory preferably, but is sometimes sent to the lead blast furnace.

9. *Old Retorts and Cupel Bottoms*.—These are added to the charges for the lead blast furnace.

**Parkes Plant Layout.**—The flow sheet of a typical, efficiently arranged refinery using the Parkes process with a small Pattinson division, built for a monthly capacity of 5,000 tons of lead bullion, is shown in Figs. 55 and 70.

**The Pattinson Process.**—This method of desilvering lead is based upon the fact that when molten, low-grade, silver-bearing lead is cooled to its freezing point, crystals of lead separate out which are much poorer in silver than the still liquid original lead. If these crystals are removed and the procedure repeated, always adding fresh lead of same tenor in silver, the bulk of the original bullion can be obtained in the form of market lead low in silver, leaving the balance in the form of an enriched lead ready for cupellation. By the repeated meltings and crystallizations involved, many of the impurities will be oxidized and collected in drosses, and the market lead correspondingly purified. A point will be reached eventually, beyond which the enrichment of the liquid lead cannot be carried. The process stops automatically, in practice, when the silver contents of the liquid lead reach 450 to 500 oz. of silver per ton; this material then going to the cupels.

Gold follows the silver. Of the base metals commonly found in lead bullion, Sb, Ni, and Bi are also concentrated in the liquid lead; As in the crystals; Cu, which



has not been removed in the softening furnace, or by drossing, remains equally distributed between the liquid and crystal lead.

The process may be conducted in one of two standard systems, the method by thirds or the method by eighths. In the first, and more common method, two-thirds of the lead in the kettle is withdrawn in the form of crystals, one-third remaining as richer liquid lead. The crystals in this case will be about half as rich in silver, and the liquid lead about twice as rich as the original bullion. In the second system, seven-eighths is taken out as crystals, one-eighth remaining liquid, and the silver in crystals will be about one-third as rich, and in the liquid lead about six times as rich as the original bullion.

The original hand-labor Pattinson process was, until recently, in use in England, and Germany. Machinery has been introduced to reduce the labor of withdrawing crystals and ladling out the liquid lead, the two principal mechanical modifications of the original process being the Luce-Rozan and the Tredinnick. In both, the metal is stirred by steam and the liquid drawn off, leaving the crystals in the kettle.

The procedure of the original process, using the method by thirds, is as follows: The kettles, varying in number from eight to fifteen according to the richness of the bullion, are arranged in a row, the position of the charging pot, or kettle in which the work lead is first melted down, varying in accordance with the proportion of silver in the lead. The pots being numbered in series, from the market lead end upwards, the charging pot may be, in, say, a series of twelve pots, anywhere between No. 6 and No. 10.

The melted bullion in the charging pot is poled and drossed, and the fire withdrawn and transferred to the next pot, in the melting stage. Crusts forming at the sides of the pot are pushed down into the lead to be remelted, and the bath is continuously stirred in order to insure uniform cooling throughout. As crystals form, they are lifted, drained, and transferred, when dry, into a neighboring pot, usually "down the house," to the right. This continues until two-thirds of the contents of the charging pot have been removed, when the remaining one-third of still liquid lead is ladled into the adjoining pot, "up the house," to the left. If there is then on hand, from previous operations, lead equal in silver contents with that in these two right and left pots, respectively, an exactly similar operation is commenced with each of these simultaneously. The charging pot thus becomes filled from the crystals of the kettle at its left and the liquid lead of the kettle at its right. In this same manner the operations are continued, the kettles "down the house" decreasing in silver tenor and the kettles "up the house" increasing, until the silver content of the lead in the market kettle at the extreme right is 0.3 to 0.5 oz. per ton, and that of the liquid lead at the extreme left is at the maximum, of about 500 oz. Before the whole plant can be in working order quite a number of crystallizations must be performed in order to have on hand the necessary amounts of lead of different silver contents required to fill the several kettles.

**The Luce-Rozan Method.**—In this modification of the Pattinson process, steam is used for stirring, and the apparatus and the arrangement of plant are of radically different nature. The plant is shown in Figs. 71, 72, and 73, and consists of two melting pans *a*, one crystallizing kettle *b*, and two large conical molds (Fig. 75), instead of the long line of some twelve kettles of the original Pattinson arrangement. The two cast-iron melting pans, used alternately, each holding 7 tons of lead, can be raised by means of a steam crane, so as to pour their contents into the crystallizer, which holds 20 tons.

The mode of working is as follows: The bullion is melted down in one of the melting pans, drossed, and run into the previously heated crystallizing kettles by raising the

back end of the pan. In the crystallizer it is stirred by steam at 45-lb. pressure, cooled by withdrawal of fire and by water sprays, and two-thirds of the contents become crystallized. The still liquid lead is then run into the conical molds from the crystallizer, and the fire under the latter replaced and the crystals ( $13\frac{1}{2}$  tons) remelted.

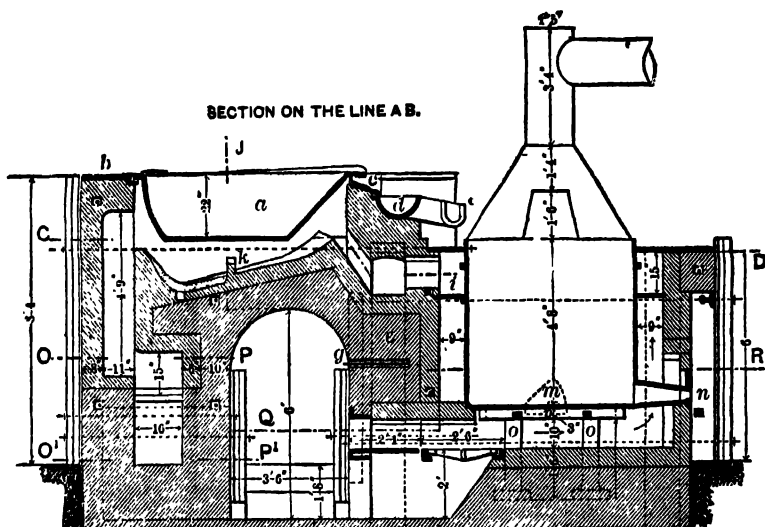


FIG. 71.—Lucco-Rozan plant.

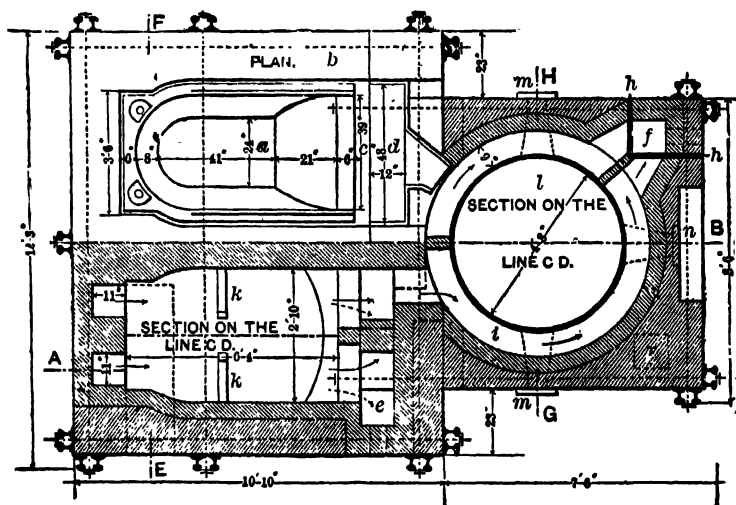


FIG. 72.—Lucco-Rozan plant.

In the meantime,  $6\frac{1}{2}$  tons more lead, with the same silver contents as that in the crystallizer, have been melted down in one of the pans, so that, as soon as the crystals have been remelted, it can be run in and a new operation begun. The other melting pan contains lead equal in silver content to the crystals which it is expected will be

produced from the next operation, and this second pan is being melted down in readiness for the next following crystallization.

Eleven crystallizations are necessary to obtain market lead from lead bullion averaging 146 oz. of silver per ton. Six charges are run in 24 hr. Two men per shift attend to the crystallization, all lead handling being done by a crane man and helper. As in the hand Pattinson process, a number of preliminary crystallizations—sixty-six at Příbram, Czechoslovakia—must take place to furnish the necessary intermediary grades of lead for normal work.

Products of the process (from above bullion) are rich lead of about 262 oz. of silver per ton, desilverized lead of about 0.43 oz. per ton, dross, and flue dust. The rich lead is cupelled, the desilverized lead is refined in a reverberatory furnace to remove arsenic and antimony and then molded into market bars, and the dross and dust are worked up with similar by-products from other parts of the works. A curious by-product sometimes encountered in the steam Pattinson process, is a small incrustation of minium—red lead—which forms in the crystallizer, produced by the action of steam on the lead at a temperature just below redness.

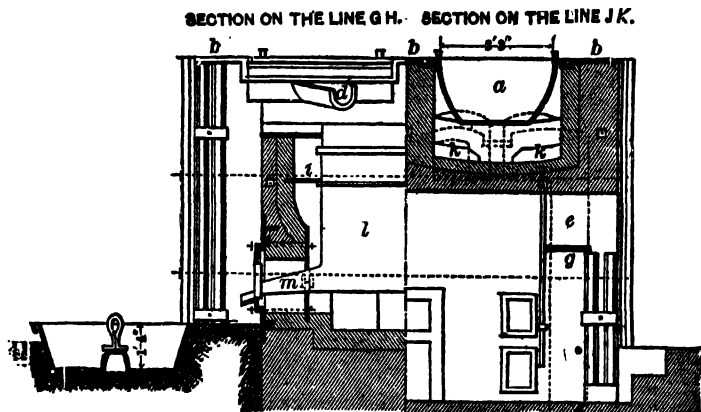


FIG. 73.—Luce-Rozan plant.

The Luce-Rozan method runs into greater plant cost and maintenance than the original Pattinson, but its advantages more than offset these items. Softening of the lead bullion is not so imperative; the cost of labor is only 30 per cent, and of fuel 40 per cent, of the Pattinson cost; and only about one-third of the amount of drosses obtained in the Pattinson cycle is produced in the Luce-Rozan.

**Tredinnick Method.**—This modification of the Pattinsonizing process is in part a combination of the original Pattinson and the Luce-Rozan processes. It has a crystallizer for each grade of lead, as has the Pattinson; it stirs with steam and drains off the liquid lead instead of transferring the crystal portion, as does the Luce-Rozan: The point of improvement consists in the use of 50-ton crystallizing kettles, twelve in number for 300-oz. bullion, each of which is mounted on a hydraulic ram so that it can be raised at will and the liquid lead run out into the adjoining kettle. Heating by gas is carried out by means of a brick-lined jacket round the kettle. Each crystallizer has two outlets, that on the left for running out the liquid lead being a double orifice, with a strainer to hold back the crystals, while that on the right permits the free running out of crystals after they are



remelted. The cycle of operations is much the same as in the original hand-Pattinson process.

The Tredinnick-Newnam apparatus for this method, used at Omaha, Neb., is shown in Figs. 76, 77, and 78. This installation was built for the purpose of recovering bismuth from lead which had been desilverized by the Parkes process. The Tredinnick process is not, at the present time, in use for desilverizing.

**Thum Process.**—It has been proposed, although the process is not in use, to transfer the content of stationary Pattinson kettles from one to another by means of compressed air through pipes heated by electric-resistance coils wound about them.

**Comparison of Pattinson Processes.**—The comparative performance of the three methods is about as follows, in point of dispatch: With the original Pattinson process using 10- to 15-ton pots only three or four operations are accomplished in 12 hr.; with the Luce-Rozan process, using 50-ton kettles, five operations may be performed per kettle in 12 hr.; with the Tredinnick process, using 50-ton kettles, about twelve to sixteen operations can be performed in an 8-hr. shift.

**Cupellation.**—The rich leads from the Pattinson process, containing 250 to 600 oz. of silver per ton, and the Parkes, containing 2,000 to 5,000 oz., are finally treated by cupellation for the separation of the precious metals. This process consists essentially of melting the rich lead in a reverberatory furnace, and exposing it to a blast of air, by which the lead and the base metals are oxidized and slagged off in the form of litharge of varying degrees of purity, while the silver, having scarcely any affinity for oxygen, remains behind in metallic state. The oxidation is accomplished mainly by the action of the air blast, and partly by the action of the molten litharge, which absorbs an excess of oxygen and gives it off to the underlying impurities Cu, As, Bi, Ag, and Au. The cupellation of gold-silver-lead and parting of doré bullion are discussed elsewhere in this volume.

## CHAPTER XXVI

### TREATMENT OF ELECTROLYTIC SLIMES AND ZINC CRUST

BY WALTER C. SMITH<sup>1</sup>

**Scope of Section.**—In this section will be given the treatment of electrolytic slimes, zinc crusts, and other highly argentiferous and auriferous by-product material.

**The zinc crusts** produced in the Parkes process of lead desilverizing are liquated in some form of liquation apparatus for the removal of the excess lead contained in the crusts. Three methods of liquation have been used: liquation in kettles; liquation in reverberatory furnaces; and pressing of the crusts in a Howard alloy press.<sup>2</sup> The last method has replaced the other two.

The pressed zinc crusts are broken into small pieces while still hot, and are usually treated by distillation for the removal and recovery of the zinc in the manner originated by Parkes. Many other methods for the treatment of zinc crusts have been tried, but the distillation method is the only one in extensive use today. The other methods may be listed as follows: smelting of the crusts in a blast furnace; direct cupellation of the crusts: fusion of the crusts with alkali chlorides; and their treatment with steam for the oxidation of the zinc and some of the lead, which process yields a rich lead for cupellation. All these methods have a common fault which is not possessed by the Parkes method, namely, the zinc is not recovered.

The process has been improved upon from time to time but, in general, is the same as that used by Parkes. The introduction by Balbach<sup>3</sup> of the use of graphite retorts has been the greatest improvement on the original method.

The Faber du Faur retort furnace is almost universally used for this work. This furnace is cubical in form, built of fire brick supported in a cast-iron frame. This frame swings on trunnions and permits the furnace to be turned over for emptying and cleaning. The furnace may be coal, coke, gas, or oil fired, but oil is the fuel most widely used. The graphite retort is supported on a small brick pier carried in the furnace, and is so placed that the mouth of the retort projects through the front wall of the furnace. The angle of inclination used for the retorts is slightly less than 30 deg. from the horizontal position. The products of combustion are removed from the back of the furnace near the top and pass to a flue, which may serve several furnaces.

The graphite retorts are pear shaped and of various sizes, some of the earlier ones having a capacity of 250 lb. of crusts; 1,500-lb. retorts are now in use. The correct placing of the retort in the furnace has a considerable bearing on the life of the retort and upon the speed of distillation.

The condensers may be made of graphite, clay, or cast-iron, old retorts being often used for this purpose. The condenser is supported either by chains at the front of the furnace, or by a special truck and stand. The joint between the retort and condenser is luted with clay. The condenser has a tap hole for the removal of molten zinc, which

<sup>1</sup> Chem. Met. Eng., Baltimore, Md.

<sup>2</sup> U. S. patent 563769, and subsequent patents. See p. 916, this book.

<sup>3</sup> EURICH, *Trans. A. I. M. E.*, **44**, 741 (1912).

is closed with a clay plug during the distillation, and a vent opening near the top for the escape of gases.

The distillation is conducted approximately as follows: the broken zinc crusts, mixed with 1 to 3 per cent of charcoal or coal, are charged to the retort by means of a small scoop or shovel. The temperature is raised to about 1200°C. as rapidly as possible; the crusts soften and are pushed down; more crusts are added until the retort has received its full charge. The condenser is then placed over the mouth of the retort and the joint is luted with clay. The distillation requires from 6 to 8 hr., but blue powder and metallic zinc begin to collect in the condenser in 30 to 40 min. after the retort has been charged. The operating temperature is between the limits of 1000 and 1300°C., although zinc boils at 918°C. At the lower temperatures the distillation is slow and much blue powder is formed in the condenser; higher temperatures yield more metallic zinc, give a faster distillation, and leave less zinc in the rich lead remaining in the retort at the end of the distillation. At 1100°C. the condensed zinc will carry 0.25 per cent of lead, and it usually carries 4 to 12 oz. of silver depending on the rate of distillation.

Tellurium remains largely in the retort bullion and clinging to the iron condenser, if one is used. The blue powder also runs high in it at times. The zinc is tapped from the condenser from time to time during the distillation and is cast as zinc slabs. When no more zinc is caught in the condenser the distillation is completed, and the condenser is removed and cleaned. The retort is then emptied by pouring the metal into a brick-lined slag pot or other suitable receiver, and the metal is transferred to a cupel furnace, a small reverberatory furnace, or is cast as bars when sufficiently cool. The retort is then scraped clean and is ready for a new charge.

The recovered zinc amounts to about 10 per cent as metal and 1 per cent as blue powder of the weight of the crust treated. The rich lead amounts to from 70 to 80 per cent of the weight of the crust charged to the retort, and carries from 4 to 10 per cent of silver and from 0.75 to 1.50 per cent of zinc. The recovery of metallic zinc is from 60 to 80 per cent of the total zinc used for desilverizing the lead bullion. The blue powder is returned to the retorts or is sold as blue powder. Retorts last from twenty-five to forty charges. One ton of zinc crusts requires from 40 to 70 gal. of oil, with air to atomize the oil depending upon the size of the retort used. Oil firing is more severe on the retorts than coke firing, but the constant danger of a retort leaking makes it advisable to smelt all the coke ashes from the retort furnaces in a blast furnace, so oil has an advantage here. One man per shift can handle from two to four retorts.

**Cupellation of Rich Lead.**—"The rich lead from the retorts and the work lead produced by the Pattinson process of lead refining are treated for the recovery of the gold and silver by cupellation. Two types of cupellation furnace and methods of operation are used: German cupellation and English cupellation.

German cupellation employed a reverberatory furnace having a fixed hearth and a movable roof; all of the bullion to be cupeled was charged at once, and the silver-gold alloy was not refined in the same furnace in which the cupellation was carried on. The German cupellation furnace has been almost entirely replaced, however, by the English furnace. The operation of the German cupel was usually conducted as follows: preparation of the hearth; charging and melting; softening; cupellation; removing and refining the crude silver. A new hearth of marl, or a mixture of crushed limestone and clay, was placed in the furnace at the beginning of each cycle. The entire charge of rich lead was then piled on the hearth, the furnace roof moved and luted into place, and the fire started. The lead was melted slowly and the dross was skimmed

<sup>1</sup> HOFMAN, H. O., "Metallurgy of Lead."

off as it formed; the temperature was raised, and the cupellation was continued until the crude silver remaining in the furnace had brightened. The crude silver was then cooled and solidified with water, broken from the hearth, cleaned, weighed, and transferred to a second furnace for refining. The old hearth material was removed, and those portions of it which contained litharge were smelted in the blast furnace, while the balance of the material was mixed with new hearth material for the next hearth.

English cupellation is conducted in a reverberatory furnace with a removable hearth and a fixed roof; the bullion to be cupeled is charged gradually, and the silver is usually refined in the same furnace.

The furnace, as used today, differs considerably from the earlier forms, but the principle of operation is the same. The fire box, or combustion chamber if oil fired, the side walls, roof, end walls, and flue are supported independently from the hearth or test, as it is called, and form a permanent structure. The test is carried on a truck which can be removed from under the fixed portion of the furnace. The roof lines of the English cupellation furnace are such as to force the heat down on to the test. The products of combustion are removed at a point directly above the litharge channel and operating door. The furnace wall opposite to the litharge channel usually has several openings, through which the tuyère pipes are introduced; an opening for the charging of the rich lead bars is also provided.

The test consists of an oval or rectangular ring of boiler iron or cast iron, resting on a cast-iron plate which is supported on two rails or steel beams. At one end these beams are carried by jackscrews, or other suitable means for lifting, and at or near the other end the beams rest on a bearing bar. The assembly is mounted on a truck which permits the entire test to be removed from the furnace and a new one substituted for it. Water-cooled tests have been used but are not necessary, though a small water-cooled jacket at the litharge channel is sometimes advisable.

**Hearth Material.**—The original English tests were made with the hearth of bone ash. This material has not found favor in America, as it is not suitable for large tests and is too expensive. The test material which has found the greatest use is a mixture of 6 parts of limestone and 1 part of clay by volume. The mixture is ground to pass from a 5- to 12-mesh screen and is then moistened with water. The moisture is disseminated through the mixture by repeated turning and mixing with shovels. The proper amount of moisture is determined by pressing a handful of the mixture; the material should form a lump which does not crumble when the pressure is released, but should not stick to the hand. If it sticks to the hand the mixture is too wet. Portland cement or a mixture of cement and ground brick have given good results as a test material. A number of other mixtures have been used at various plants, and a test lined with magnesite brick has been used successfully.

The test is lined in several ways. One method is to add enough of the test material to form the bottom, and to tamp this in place, either as one layer or as several layers; a wooden or metal form is then placed on the bottom and the material is tamped in between this form and the test ring to form the sides of the test. A second method is to add all of the material to the test, then place a skeleton form in the test, and tamp the bottom and sides at the same time.

The making of a test requires considerable experience; too much tamping gives a test which is hard and will crack; too little tamping gives a soft test which will absorb too much lead; too little water in the mixture gives a test which will peel; and too much water in the mixture will not permit the proper tamping of the material. The finished test is allowed to dry slowly for several days, if possible, before being placed in service.

**Operation of the Cupellation Furnace.**—The test is put in place and the furnace is slowly heated; when it has reached a dark-red heat, sufficient lead to fill the test is charged and melted down. The temperature is brought to a cherry-red heat and the blast is turned on through the tuyère pipes. The litharge formed is drawn off at the litharge channel, and more rich lead is supplied at the back of the test through openings provided in the furnace wall for that purpose. The lead is added at a rate which will keep the lead level in the test nearly constant. The withdrawal of the litharge is so regulated by tilting the test, or by the addition of lead, that approximately one-half of the surface of the molten lead remains covered with litharge. The litharge is collected in cast-iron pans or pots, mounted on wheels. The tuyère pipes are adjusted so that the air blasts converge and force the litharge toward the litharge channel. If too much molten lead surface is exposed to the action of the blast the litharge will carry excessive silver, and the loss of lead and silver by volatilization is increased; if too much of the surface of the lead is covered by the litharge the cupellation is retarded. The rich lead is fed to the test until the test is filled with metal which has been concentrated to 60 to 70 per cent silver, at which point the refining operation begins. The refining can be done in the same furnace, or the metal can be cast as bars and refined in a second furnace.

**Refining.**—The refining operation is the same as the concentration, except that toward the end of the refining period the temperature has to be increased in order to keep the more infusible silver-lead alloy molten. The last of the litharge is drawn off by tilting the test by means of the jacks of the test carriage, leaving the crude silver or doré exposed to the action of the heat and air blast. The metal is sampled from time to time to show the progress of the refining process. Sodium nitrate is sometimes used to remove the last of the impurities from the metal. Often a few bars of pure lead are added and the refining operation is repeated several times. The refined metal should assay 995, or better, parts per thousand of gold plus silver, and is then cast in the form of thin plates for parting by either the acid or electrolytic method.

The loss of lead during cupellation of rich lead will average about 5 per cent of the weight of the lead charged to the test; the silver loss will average about 1 per cent; and the gold loss will be small, except when treating an alloy which is rich in gold. The gases from the cupel furnaces are usually passed to a bag house or a Cottrell treater for the recovery of the fumed metals, thereby reducing the losses considerably.

**Life of the Tests.**—Tests made of limestone-clay mixtures often last for 15 to 30 days when used for concentrating only, and from 3 to 10 days when used for refining only. The bottom and sides of the test gradually become thin and the test has to be changed. Water-jacketed tests, filled with the limestone-clay mixture, have lasted for 60 days when used only for concentrating. The lining of an old test is broken out with bars and hammers; the metallic silver is picked out and returned to the cupel; and the old lining is smelted in the blast furnace.

One man on each shift is required for the operation of each cupel. The fuel required varies with the size of the cupellation furnace; as, for example, a test holding from 1,500 to 2,000 lb. of retort bullion will treat about  $6\frac{1}{2}$  tons of bullion per 24 hr. and uses  $1\frac{1}{2}$  tons of coal; a smaller furnace, holding 1,000 lb. of bullion, will treat  $3\frac{1}{2}$  tons of bullion per 24 hr. and uses  $1\frac{1}{2}$  to 2 tons of coal. The refining operation usually requires from 5 to 7 hr. and uses about 1,500 lb. of coal. The oil consumed by oil-fired furnaces is proportional to the coal used with coal-fired furnaces.

**Impurities.**—The impurities found in retort bullion are, as a rule, Cu, As, Sb, Bi, Te, and Zn.

Copper in the bullion is gradually taken up by the litharge, but if present in the bullion in large quantities some copper will often remain in the metal until the refining stage is reached. The presence of a small amount of  $\text{Cu}_2\text{O}$  in the litharge during the concentration stage seems to increase the speed of cupellation. The probable explanation of this is that  $\text{PbO}$  and  $\text{Cu}_2\text{O}$  form an eutectic which makes it possible to cupel at a lower temperature than would be possible if  $\text{Cu}_2\text{O}$  were absent.

Arsenic and antimony are partly volatilized and partly oxidized, and are removed in the litharge. They have no special influence on the cupellation.

Bismuth is concentrated with the silver until toward the end of the operation, and then begins to oxidize and is carried off with the litharge. The last traces of bismuth are difficult to remove from silver or doré. Some bismuth is absorbed by the test, and, if bismuth is to be recovered, the test material and the bismuth litharge are retreated separately for the bismuth.

Tellurium tends to remain with the silver and is the most difficult of all the common impurities to remove. Repeated refining with lead and the use of sodium nitrate or caustic soda are the most effective means for its removal. Tests have shown that about 60 per cent of the tellurium in bullion enters the litharge; 37 to 38 per cent is volatilized, and about  $1\frac{1}{2}$  to 2 per cent remains in the metal.

Zinc is readily oxidized and passes into the flue products, or is carried off with the litharge. Platinum and palladium in the rich lead, or in material charged to the cupels, are collected and retained by the silver or doré and are recovered in the refining of the gold.

#### TREATMENT OF ELECTROLYTIC SLIMES

**Treatment of Copper Slime.**—The slime produced in the electrolytic refining of copper varies in both quantity and composition with the kind and grade of anode metal refined. Most of the refineries attempt to blend and refine the pig copper in the anode-casting furnaces in order to secure anode metal assaying about 99 per cent copper. The yield of slime from this grade of anode metal should average between 1 and 2 per cent of the weight of anode dissolved. Typical examples of copper anode slime are given in the following table:

	1	2	3	4	5	6	7
Ag, ounces per ton	6,220 4	4,680 5	14,012 8	8,238 5	9,631 5	927.90	310.5
Au, ounces per ton	143 6	64 5	91 7	107 5	96 55	402 75	10.15
Cu, per cent . . . .	18 24	28.09	13 53	23 89	4 47	69.03	46.53
Ni, per cent. . . . .	1 63	2 64	0 54	0.40	0.27	2.03	23.13
As, per cent . . . . .	0 32	1 12	2 16	2.86	1 97	0.15	0 28
Sb, per cent . . . . .	4 56	3 54	3 04	3.76	7.20	0.15	0.68
Bi, per cent . . . . .	Trace	None	Trace				
Se, per cent. . . . .	18 05	16 14	4 27	5.60	1.15	0.85	6.60
Te, per cent . . . . .	2 36	2 21	1 07	1 95	0 85	1 50	0 27
Pb, per cent. . . . .	4 95	1 93	8.83	6.71	25.34	0 79	1.53
Zn, per cent . . . . .	Trace	Trace					
S, per cent. . . . .	3 31	4 09	5 31	4 64	4.99	15 41	1.58
Fe, per cent. . . . .	0 41	0 53	0 38	0.40	0.25	1.04	0.41
$\text{SiO}_2$ , per cent. . . . .	4 27	6 35			0 43	0 41	0 93
Sn, per cent . . . . .	1 05	0 23			0 15	0.09	0.31

Samples No. 1 to 5 were composite samples of the slime from at least 10,000 tons of anodes. Sample No. 6 was taken from a run made on low-silver, high-gold anodes; sample No. 7 was taken from a run on high-nickel anodes.

Slimes-treatment processes,<sup>1</sup> to be successful, must fulfil several requirements which may be listed as follows: minimum metal loss; prompt delivery of the bulk of the gold and silver; delivery of the by-products in a recoverable form; economy of operation; and the introduction of no chemicals to the process which may have an injurious effect on the refining of copper.

In the early days of electrolytic refining the slime was screened to remove metallic copper; washed to free it of soluble copper salts; filtered to remove excess water; and cupeled with lead in a cupel furnace. The lead loss was heavy and the litharge was fouled with copper. It was discovered that much better results were obtained in the furnace work with a slime from which the copper had been removed.

**Copper Removal.**—The first method employed for the removal of the copper from screened raw slime was to boil the slime with dilute sulphuric acid to which sodium nitrate was added in small doses. The boiling operations were conducted in lead-lined tanks equipped with paddle or air agitators; the slime was run into the tank and enough sulphuric acid was added to make a 50 per cent sulphuric acid solution; the mixture was then heated with steam to the boiling point, and the sodium nitrate was added a few pounds at a time. Heavy fumes of poisonous, nitrous gases were given off, and if the sodium nitrate was added in too large doses the charge would foam over the top of the boiling tank. It often required 48 to 72 hr. to reduce the copper in the treated slime to 2 to 3 per cent. The lead tank lining was rapidly attacked and needed frequent repairs. The copper solution from the slime leaching was settled to remove the last traces of suspended slime and added to the tank-house electrolyte. So long as the electrolyte purification system withdrew a large volume of solution for the manufacture of copper sulphate, no trouble from sodium compounds in the electrolyte was experienced, but with the decreased market for copper sulphate and the cyclic purification methods later developed, the sodium salts accumulated in the electrolyte and caused trouble.

The raw slime was also treated for the removal of copper by boiling with a 50 per cent sulphuric acid to which manganese dioxide was added in small quantities at a time, until the copper had been oxidized and dissolved. The addition of an excessive amount of the manganese dioxide at one time would cause the charge to foam over the top of the boiling tank. The copper solution from the boiling of the slime contained manganese sulphate, and this solution could not be added to the regular electrolyte as the manganese salt caused trouble in the electrolytic cells. The solution was, therefore, sent to the copper-sulphate plant and was used for the production of blue stone. The manganese salts eventually went to waste in the spent liquors from the iron cementation tanks in which the last of the copper was precipitated from the mother liquors. These methods have been superseded by one of the several forms of either oxidizing roast or sulphatizing roast, following by leaching with dilute sulphuric acid or water.

**Oxidizing Roast.**—When screened raw slime is subjected to an oxidizing roast, most of the copper is rendered soluble in dilute sulphuric acid. The temperature

<sup>1</sup> ADDICKS, L., "Copper Refining," p. 107.

of the roasting depends upon the character of the slime which is being treated. The copper in some slime is rendered soluble by merely drying the slime at 105 to 110°C.; other slime requires roasting or baking for 8 to 15 hr. at a temperature of 175 to 200°C.; some slime can be roasted at 250 to 300°C.; and still other slime may require a temperature of 500°C. to render 95 per cent of the copper soluble. The roasting of copper slime at higher temperatures usually renders some silver and selenium soluble in the dilute acid.

The roasting may be done on the hearth of a roasting furnace, or in pans or trays placed in special roasting furnaces.<sup>1</sup> One refinery pumps the raw slime, which has been thickened but not washed free of soluble copper and acid, to the hearth of the roasting furnace where the slime is first dried and then roasted, thereby eliminating the time and cost of washing and filter pressing the raw slime. The roasting temperature employed is below the point at which the slime begins to frit, and the time required for the roast varies from 5 to 15 hr.; the lower the temperature employed the longer the time.

The following examples<sup>2</sup> show the manner in which different slimes act during the roast and the leach with 40 per cent sulphuric acid.

Sample	1	2	3	4	5
Ag, ounces per ton	3,003 0	11,373.9	927 9	310 5	1,506.8
Au, ounces per ton	66 02	13 1	402 75	10.15	13.7
Cu, per cent..	41.64	13.57	69 03	46.53	59.17
Ni, per cent....	0 12	0.14	2 03	23 13	2.40
As, per cent	1.12	1 61	0 15	0 28	0 50
Sb, per cent	0 72	9 48	0.15	0 68	0.25
Se, per cent	18 70	0 25	0 85	6 60	4.72
Te, per cent	0 82	0 10	1 50	0 27	1.15
Pb, per cent	2 89	9 48	0 79	1.53	2 32
S, per cent...	4 85	6 11	15.41	1 58	13 54
Fe, per cent.	0 31	0.42	1 04	0 41	0 67
Sn, per cent...	0 29	0 11	0 09	0 31	0.43

<sup>1</sup> U. S. patent, 1085831, R. T. Wales

<sup>2</sup> Personal notes.



Sample	Roast, 6 hr. at, in degrees Centigrade	Per cent soluble Cu	Soluble Ag	Soluble Se
1	140	70.40	No	No
1	250	75.00	No	No
1	300	82.40	No	No
1	400	99.83	Yes	Yes
2	140	89.10	No	No
2	250	96.14	Yes	No
2	400	98.53	Yes	No
3	140	12.34	No	No
3	250	71.96	No	No
3	400	91.96	No	No
3	500	96.53	Yes	No
4	200	31.16 6.73 Ni	No	No
4	300	67.90 10.57 Ni	No	No
4	400	91.58 38.62 Ni	Yes	No
4	550	99.30 11.53 Ni	Yes	Yes
5	140	18.80	No	No
5	200	24.60	No	No
5	300	30.30	No	No
5	400	94.45	No	No
5	500	99.90	Yes	Yes

The roasting experiments were conducted in an electric furnace of the wire-wound tube type, slightly inclined for the purpose of inducing a draft of air through the furnace to insure a plentiful supply of oxygen. The temperature of the electric furnace could be regulated to within a few degrees of the temperature desired.

**Sulphatizing Roast.**—Dr. Edward Keller<sup>1</sup> mixed raw slime with sufficient concentrated sulphuric acid to combine with the copper in the slime, and roasted the mixture. He employed a furnace, the hearth of which was a steel pan. The temperature of the roasting furnace was approximately 230°C. The roasted material was withdrawn from the furnace in a fairly dry condition and sent to the leaching tanks. An excessive roasting temperature caused the material to bake into hard lumps which did not disintegrate properly in the leaching operation, and hence gave a poor copper extraction; at lower temperatures the copper was not rendered soluble. The roast with sulphuric acid gave off considerable quantity of sulphuric acid fumes, and this was often objectionable unless precautions were taken to absorb or precipitate these fumes. The best results were said to be obtained if the acid was almost exactly the theoretical amount necessary to combine with the copper.

<sup>1</sup> U. S. patent, 1110493, Dr. EDWARD KELLER.

**Leaching of the Roasted Slime.**—The leaching or boiling of the roasted slime is carried out in cylindrical lead-lined tanks equipped with a paddle agitator, or in rectangular tanks having hopper bottoms and agitated by means of compressed air. The Pachuca type of tank gives very good results if agitated by means of a mixture of air and steam. The heating is done either with steam coils in the leaching tanks or by blowing live steam into the leach solutions.

The operation is carried on about as follows: the proper amount of water or weak wash liquor (in the sulphatizing roast), or the mixture of water or weak wash liquor and sulphuric acid (in the oxidizing roast), is run into the tank and the agitation started; the roasted slime is then added and the agitation continued until the slime has been completely disintegrated. The solution is then tested for the presence of soluble silver and selenium; if either or both are present, a small amount of raw slime is run into the tank and the agitation is continued; the solution is again tested, and the raw slime additions are repeated until tests show that all of the silver and selenium have been precipitated. The batch is allowed to settle, the solution siphoned off, and the slime washed several times by decantation. Weak wash water from the filter is used for the first several washes; the last wash is usually made with water. The slime is then filtered and given the final wash in the filter. The discharged filter cake carries from 18 to 30 per cent moisture and is ready for the furnace treatment unless drying is necessary. Some refineries ship the treated slime elsewhere for treatment, and in this case the slime is dried, sampled, weighed, and packed in barrels or metal-lined boxes for shipment. Steam driers or iron pans placed over a direct fire are used for drying the slime. The treated slime should not contain more than 1 to 3 per cent of copper if the roasting and leaching have been properly carried out.

At one of the refineries, the treated slime is washed in the boiling tanks by decantation until free of soluble copper; the excess liquor is siphoned off; the thickened slime is pumped to the hearth of a special roasting furnace; and is then dried and given an oxidizing roast at a dark-red heat in order to eliminate as much of the selenium as possible and to deliver an oxidized dry slime to the slime melting furnaces. The oxidized slime is mixed with soda ash before being charged to the melting furnaces. The roasting operation saves the cost of filtering and it also gives a dry charge for the melting furnaces which melts down in less time and with less fuel than would be required by wet slime or filter cake.

Silver sulphate dissolves the metallic copper and some of the combined copper in the raw slime as shown by the following experiment.<sup>1</sup> To 1,500 c.c. of dilute sulphuric acid, 10 per cent, 15 g. of silver as silver sulphate were added, and the mixture heated to boiling; weighed quantities of raw slime were added in small amounts until tests showed that all of the soluble silver had been precipitated; the residue was washed free of soluble copper, filtered, dried, weighed, and assayed for copper. The experiment was repeated, using several kinds of raw slime. In each test the residue carried only very small amounts of copper; the copper extraction from the raw slime varied from 96 to 99 per cent in the individual tests, and the average extraction for all of the tests was 98.7 per cent.

**Furnace Refining of the Treated Slime.**—The first refineries treated the boiled slime with lead in cupel furnaces, and this method is used today at those plants which refine both lead and copper. One method for charging the slime to the cupel furnace consisted in packing the slime in small paper bags which held from 15 to 25 lb. of slime, and in charging the bags of slime to the surface of the molten lead in the furnace. This method probably caused a heavy dusting loss. A better method consists in mixing the slime with litharge and a little fine coal and

<sup>1</sup> Personal notes.

smelting the mixture in a small basic-lined reverberatory furnace to a slag and metal. The metal is cast in the form of bars and is fed to the cupel as needed; the slag is smelted in the lead blast furnace. Most of the copper refineries are not operated in conjunction with a lead refinery, hence other methods of treatment were developed.

The melting of treated slime in a basic-lined reverberatory furnace yields a lead-antimony slag, called tapped or sharp slag, and a metal which consists of Ag, Au, Se, Te, some Cu, and other metals. If the slime carries considerable selenium or tellurium, a third product, a matte or speiss, in which selenium and tellurium take the place of sulphur, may be formed. This matte or speiss is a most troublesome material to handle and may carry as much as 50 per cent silver. Several methods are used either to prevent the formation of this matte, or to decompose it after it has been formed.

**Fluxing the Slime.**—The treated slime is often mixed with fluxes before charging to the melting furnace. The fluxes used are silica, lime, soda ash, salt cake, niter cake, caustic soda, or a mixture of several of these. The thin slag which is formed is tapped from the furnace, and the metal is oxidized by forcing compressed air under the surface of the metal through iron pipes. A second slag is formed, which is skimmed off, and the metal is refined to doré with air and niter, or niter and soda ash. When slimes carrying excessive amounts of copper, selenium, and tellurium are being furnaceed, a matte will separate from the metal during the refining process; this matte retards the refining operations and is best handled by tapping off, crushing to 10 mesh, roasting and leaching with sulphuric acid for the removal of the copper before returning to the melting furnace.

The following data<sup>1</sup> show the composition of the matte at different stages during an attempt to oxidize it in the melting furnace by means of air, niter, and soda ash. Samples were taken every 4 hr. over a period of 28 hr.

Sample No.	Au, ounces per ton	Ag, ounces per ton	Cu, per cent	Se, per cent	Te, per cent
1	139.15	13,751.8	20.67	22.83	0.50
2	105.55	14,336.0	22.88	20.80	1.20
3	67.42	14,139.3	25.33	19.34	1.35
4	25.70	12,016.0	33.07	15.25	1.52
5	18.15	9,685.1	33.81	12.05	2.48
6	10.20	8,707.9	31.83	7.67	2.44
7	6.85	8,102.5	47.32	0.62	1.20
8	5.10	7,664.9	49.40	0.15	0.07

At one plant, the treated slime is melted without flux to a sharp slag and a matte or speiss and metal in one furnace; the slag is tapped off and the metal and speiss are transferred to a second furnace in which the mixture is refined to doré with air, caustic soda, and niter.

The sharp slag from the slime-melting furnace usually carries from 0.5 to 4 oz. per ton of gold; 125 to 500 oz. per ton of silver; with varying amounts of copper, lead, and antimony. A typical slag will assay about as follows:

<sup>1</sup> Personal notes.

Oz. per ton		Per cent							
Au	Ag	Cu	Pb	Ni	As	Sb	Se	Te	SiO <sub>2</sub>
0.80	458	3.99	16.76	0.27	0.97	5.18	0.58	0.52	18.0

The sharp slag is sold to the lead smelter for the gold, silver, and lead contained in it; is smelted to copper matte in the ore-smelting furnaces and the matte blown to blister copper in converters; charged to the anode furnaces; or smelted to black copper in the copper blast furnace. The last two methods are the least desirable, since the sharp slag contains many impurities which go into the anode or the black copper and are circulated through the process. A partial elimination of these impurities is made in both the matte smelting and converting operations; hence this method of treatment gives a better elimination of the impurities, but, unfortunately, many of the refineries do not smelt sulphide ores.

Sharp slags, which contain high silver values, and the second slags, produced during the refining stage, are generally retreated in the slime-melting furnaces either with slime or in separate campaigns, and eventually report as sharp slag.

The soda-niter slags are either charged to the slime-melting furnaces with slime, or are first crushed and leached for the removal of the selenium and tellurium contained in the slime, and the leached residue is returned to the slime furnace.

**Slime Furnaces.**—Small, oil-fired, reverberatory furnaces lined with magnesite or chrome brick are used for the melting of the slime. The charge is introduced at intervals, and each batch is melted down before the next charge is made. Sharp slag is often tapped from the furnace several times before the furnace is fully charged. It is customary to add a small amount of coal to the slag, from  $\frac{1}{2}$  to 1 hr. before the slag is tapped, in order to secure a cleaner slag. The slime may be charged to the furnace through the regular working door by shoveling, or by dropping from hoppers through charge holes in the furnace roof. The life of a furnace bottom is from 6 to 12 months; the side walls and roof require patching about every 30 to 60 days.

Metal absorption of a furnace is almost directly proportional to the volume of the brickwork below the metal line of the furnace; hence, in order to reduce the interest on the metals tied up in furnace linings, the furnace should be of such design as to have the maximum capacity with the minimum of lining consistent with good fuel consumption and furnace life. A new type of thinly lined, cylindrical, tilting furnace has recently been developed at one of the refineries. Two small furnaces of this construction have replaced one furnace of the stationary type; each furnace melts and refines a charge of 6 to 8 tons of slime in 48 to 60 hr., while the larger furnace requires from 90 to 120 hr. to treat 12 to 15 tons of slime. The two small furnaces absorb less metal than the single larger furnace, and also make an interest saving of from five to six days on the metals in process. This saving is made by the reduced time the slime is waiting for furnace treatment, the reduced time the metal is in the furnace, and the reduced time the doré is awaiting parting because of the delivery of very large batches to the parting plant necessary with the large furnace.

**Metal Losses.**—The gases from the slime-roasting, -melting and -refining furnaces contain Ag, Au, As, Sb, Se, and Te; hence some method for the recovery of the values from the furnace gases is necessary. The losses are due both to volatilization and mechanical dusting of the charge. As much as 1.25 per cent of the silver in the slime treated has been recovered from the furnace gases. The earlier plants used settling chambers and water scrubbers, but these were never satisfactory. Bag houses could not be used because the acid in the gases rapidly destroyed the bags. Cottrell precipitators are used for this work with good results. The treaters may handle the gases either hot, or wet and cold. The hot treater can be made of steel, but the wet treater must be constructed of lead or other acid-proof material. The wet treaters are more expensive to build than the hot treaters, but have found the most favor. Recent consideration has been given to the use of both hot and wet-cold treaters. This combination will permit fractional precipitation and probably will give a better recovery of the value in the gases than either hot or wet treaters used alone.

The flue system at one of the refineries may be taken as more or less typical. The gases are drawn through a brick collecting flue to a brick settling flue; pass to the steel-plate fan which supplies the draft to the furnaces; are forced through two lead spray towers, in which the gases are washed with circulating solution and cooled; thence through a lead settling chamber to the Cottrell. The Cottrell consists of three units of thirty lead pipes, each 8 in. in diameter and 16 ft. long, equipped with a water-flushing system for washing the collected material from the pipes and conveying it to the settling tanks. The electrical equipment is in duplicate in order to insure continuous operation; 15 to 20 kva. are required for the operation of the treater. The treater handles approximately 12,000 cu. ft. of gas per minute at a temperature of 60 to 80°C., and recovers from 95 to 98 per cent of the silver in the gases entering the treater. The entire flue system recovers from 97 to 99.5 per cent of the silver entering the flues. The recovery is about equally divided among the settling chambers, the spray towers, and the Cottrell.

**Recovery of By-products.**—The by-products of commercial importance in copper slime are selenium, platinum, and palladium. The platinum and palladium remain with the gold and silver, are delivered to the parting plant in the doré, and are recovered during the refining of the gold. Reference should be made to the separate chapters covering these metals.

**Wet Methods for Slime Treatment.**—Much thought and money have been expended in trying to develop wet methods for the treatment of slime, and several rather promising schemes have been given large-scale tests, but no such methods are in use at the present time. The wet treatment of the slime for the removal of the copper, followed by furnace refining to doré and the parting of the doré, is far from perfect, but yields better results than any wet process known. The methods used for the treatment of the lead slime produced by the Betts process of lead refining are given on pp. 1092 to 1094, Electrolytic Refining of Lead, and pp. 849 to 851, Bismuth.

**Treatment of Electrolytic Tin Slime.**—The American Smelting & Refining Co., at the Perth Amboy, N. J., plant, at one time operated an electrolytic tin refinery. Very little information relative to the process has been given out. It is known that the impure tin treated carries lead, bismuth, and silver as the chief impurities. The slime undoubtedly contains considerable tin, as well as the other metals,

and if the slime were to be charged to the cupel furnaces this tin would be lost. Some method for the removal of the major portion of the tin from the slime probably has been developed, and the lead, bismuth, and silver residue could then be shipped to the Omaha, Neb., plant for the recovery of the bismuth.

#### **OTHER SILVER- AND GOLD-BEARING MATERIALS**

**Treatment of Cyanide Bullion.**—The silver bullion produced by the cyanide treatment of silver and silver-gold ores is often refined and parted at the large refineries on a custom basis. The bullion is weighed and sampled, either by drill sampling or by melting and dip sampling, charged to the cupel furnaces or the slime-refining furnaces, and refined to a suitable doré for parting.

The cyanide precipitates at Pachuca, Mex., are first treated with dilute sulphuric acid to remove as much zinc as possible; are then melted in a basic-lined reverberatory furnace; and are refined with air to a very high-grade doré for electrolytic parting. Low-grade cyanide precipitates are treated at some of the lead refineries by mixing with litharge and a small percentage of coal, and smelting to a rich lead, which is then treated in the cupel furnaces.

Sulphide precipitates are handled in the same manner, except that no coal is used in the mixture; the sulphur in the precipitates reduces sufficient litharge to metallic lead to collect the values. The litharge slags from this furnace are retreated in the lead blast furnace.

**Jewelry Sweeps and Other Industrial Wastes.**—These materials are usually in a very finely divided state when received, and are sampled and graded into two classes according to the assay value. High-grade material is often charged directly to the cupel or slime furnace in order to get the bulk of the precious metals on the market as soon as possible. The low-grade materials are sintered, briquetted, or nodulized with other fine material and smelted in either lead or copper blast furnaces. The lead bullion or copper matte, or both, serve as the collector for the precious metals, and these products are treated for the precious metals they contain. The rich lead is either desilverized by the Parkes process or, if sufficiently rich, is sent to the cupels directly. The copper matte is blown to blister copper in converters and refined electrolytically; or the converter copper is shot by pouring in a thin stream into water; the shot copper is dissolved in shot towers or oxidizers by sulphuric acid; the copper is crystallized as blue stone, and the insoluble residue from the shot copper is treated in the cupel or slime furnace for the values contained in the copper.

A general rule not always observed in the treatment of very rich material is that it is often wise to make chemical perfection subservient to saving interest charges on the metals tied up in the process.

## CHAPTER XXVII

### THE METALLURGY OF COPPER

BY FRANCIS R. PYNE<sup>1</sup>

**The ores of copper** may be classified under three main groups: native copper ores; oxide ores; sulphide ores. Native copper ores occur principally in the northern part of Michigan, and in three main forms: vein deposits, in which the copper occurs at times in enormous masses; amygdaloidal diabase, through which copper is disseminated; conglomerate, in which the cementing material consists, to a degree, of metallic copper. Native copper also occurs in China to a small extent. In Chile it occurs as copper *barilla*, in which the fine metallic particles are disseminated throughout sandstone.

The principal oxide ores are malachite ( $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ ); azurite ( $2\text{CuCO}_3 \cdot (\text{CuOH})_2$ ); cuprite ( $\text{Cu}_2\text{O}$ ); atacamite ( $\text{CuCl}_2$ ); and brochantite ( $\text{CuSO}_4 \cdot 3\text{Cu(OH)}_2$ ). The oxide ores form much of the bulk of the South American and African copper supply. The principal sulphide ores are chalcocite ( $\text{Cu}_2\text{S}$ ); chalcopyrite ( $\text{Cu}_2\text{SFe}_2\text{S}_3$ ); covellite ( $\text{CuS}$ ); bornite ( $3\text{Cu}_5\text{SFe}_2\text{S}_3$ ); and to these should be added copper-bearing pyrite ( $\text{FeS}_2$ ).

The sulphide ores, however, furnish the bulk of the copper supply of the world, though the oxide ores are rapidly increasing in importance. At the mine the ores may be separated into high and low grade, the first containing such a percentage of copper that it is economical to treat it without further preparation; the second, containing such a small amount of copper that it becomes necessary to give it a further mechanical concentration in order to extract as much of the worthless rock as possible before treatment, and avoid the excess payment of freight, slagging, and accompanying metal losses. For the various methods of mechanical concentration refer to Chap. VI.

**Smelting of Sulphide Ores.**—In the smelting of sulphide ores, which may be considered as mixtures of copper and iron sulphides accompanied by siliceous or basic gangue, advantage is taken of the strong affinity of copper for sulphur and its weak affinity for oxygen, in comparison with the other bases in the ore. The object of smelting is to cause by fusion the conversion of the gangue into as valueless a slag as possible by the addition of proper fluxes, and at the same time concentrate the copper and other valuable constituents of the ore into a small amount of high-grade material for further treatment.

Two important materials are formed during the smelting of copper-sulphide ores: first, the slag produced by the combination of the gangue of the ore and the added flux; second, the matte which is the product of the fusion of the metallic sulphides. Of these two products the slag receives the first consideration of the metallurgist, because the sulphides melt readily under almost any circumstances, but unless the slag-forming constituents are properly proportioned serious difficulties will result.

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A satisfactory slag must possess the following qualifications: (1) It must be as economical as possible, and to this end the other qualifications are subordinated, as a scientifically perfect slag may in the end be so expensive that any margin of profit is wiped out in its cost. (2) It must be sufficiently liquid to flow freely, but should not require an excessive amount of fuel to produce this condition. (3) The specific gravity should be sufficiently below that of the matte as to permit the latter to separate thoroughly from it.

The type of slag to be made depends, of course, upon the slag-forming constituents available, and by the following general properties of the silicates.

*Subsilicates*.—While these slags are very fluid, they have a high formation temperature, and the specific gravity is so high as to make clean settling difficult, thus causing high metal losses. In addition, they are very corrosive and destructive to furnace and settler linings.

*Monosilicates*.—These are quite fluid, but have a high formation temperature and are of sufficiently high specific gravity to make clean settling difficult. Basic silicates have a high dissolving power for metallic sulphides and thus tend to increase the metal loss in the slag.

*Sesquisilicates*.—These are mixtures of monosilicates and bisilicates, and are generally employed in smelting operations. They are sufficiently fluid to flow freely, the formation temperature is not excessive, and the specific gravity is sufficiently low to permit of clean settling with a consequent reduction of the metal loss.

*Bisilicates*.—These slags have a lower formation temperature and the specific gravity is low. But they are more or less thick and viscous unless a high working temperature is carried in the furnace, so that the slag flows freely. Consequently, they require more fuel and thus are more expensive. When used they are, however, very clean slags.

*Trisilicates*.—These are seldom met with in any metallurgical practice as they require a very high temperature for their formation, and, as they are extremely viscous, require an excessive amount of fuel in order that they may flow properly.

As silicates with two or more bases are characterized by increased fusibility and fluidity, up to a certain point, it frequently becomes advantageous to have a few per cent of lime present. Frequently, on account of a shortage of iron, it becomes necessary to replace it with lime to a considerable extent and this generally adds to the cost of the slag.

The amount of matte formed is dependent upon the amount of available sulphur in the ore. By available sulphur is meant that sulphur which is present when the temperature of the furnace is such that chemical activity commences between the copper, iron, and sulphur.

When the raw sulphides are subjected to heating in a neutral atmosphere, any sulphur in combination with copper in excess of the compound  $\text{Cu}_2\text{S}$  will be expelled, and the product of fusion will be  $\text{Cu}_2\text{S}$  which may be said to be the stable compound of copper and sulphur. Similarly with the iron sulphides, any sulphur in combination with iron in excess of the compound  $\text{FeS}$  will be expelled, and a fusion will result in the formation of this compound. Should, however, the heating be carried to a point somewhere between 1200 and 1500°C. a further amount of the sulphur is volatilized and an equivalent amount of metallic iron is set free, giving a compound that may be written  $\text{FeFeS}$ , which is of great importance in pyritic smelting.

From the above it is seen that chalcopyrite ( $\text{Cu}_5\text{SFe}_2\text{S}_3$ ) will lose about one-quarter of its sulphur by heat alone; covellite ( $\text{CuS}$ ) will lose half of its sulphur; bornite ( $3\text{Cu}_2\text{SFeS}_3$ ) will lose one-sixth of its sulphur; and pyrite ( $\text{FeS}_2$ ) half of its sulphur. For all practical purposes matte may be considered to be a mixture of  $\text{Cu}_2\text{S}$  and  $\text{FeS}$  in varying proportions. It is also an excellent collector of gold, silver, and the other precious metals.

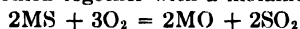


An ore high in sulphur and iron, but low in copper, will, upon fusion, produce a matte containing so low a percentage of copper that its subsequent treatment would, under ordinary circumstances, cost too much, and as it is the object of the metallurgist to concentrate the copper in his products up to the most economical point, steps must be taken to reduce the amount of sulphur available for the formation of matte and lower the amount of the latter produced per ton of ore smelted.

Such reduction may be accomplished in two ways, by an oxidizing roasting, or by subjecting the ore to an oxidizing fusion. When the ore occurs as massive sulphides, the latter method is frequently used where conditions make it economical; when the ores are not massive, the oxidizing roast is the predominating method.

Roasting is the heating to an elevated temperature, without fusion, or at least only with incipient fusion, of ores or metallic compounds in contact with oxidizing materials, in order to produce a chemical change or to eliminate a component by volatilization. In copper metallurgy, the oxidizing material is the oxygen of the air, and the object is the partial elimination of the sulphur in the ore.

When a metallic sulphide is heated to a sufficiently high temperature with access of air, sulphur dioxide is formed together with a metallic oxide.



Proper oxidation requires a temperature sufficiently high to produce the necessary affinity between the oxygen and the sulphur, but it must not be so high as to cause the surface of the ore particles to melt and form a protecting layer which retards the oxidizing action and may even cause it to cease. This temperature may be obtained by the combustion of extraneous fuel or by the heat of oxidation of the constituent of the charge.

A second requirement for proper oxidation is a constant and abundant supply of air in immediate contact with the surface to be oxidized. The necessity for an abundant supply is due to the fact that the oxidizing power of the air is lowered out of all proportion when diluted by the products of oxidation. In other words, if the air for oxidation is diluted with its own volume of gaseous products, the oxidizing effect of the resulting mixture will be much less than half the oxidizing power of pure air. The more rapidly the gaseous products are removed and replaced by pure air, therefore, the more rapid will be the roast.

The speed and the thoroughness of the roast are also governed by the size of the particles in the roaster. It is obvious that the finer the ore is crushed the greater will be the surface exposed to the oxidizing influences. However, as fine material always results in losses through handling, flue dust losses, etc., it will be seen that there is an economical point where the increased speed of roasting will be offset by the losses in material, the recovery of which necessitates expensive installations. The usual charge to a roaster consists of a mixture of relatively coarse and fine particles, and the roast is carried to a point where the overroasting of the fine particles balances the underroasting of the coarse particles, so that the final mixture from the roaster gives the desired sulphur content. The various types of apparatus used in roasting copper ores may be roughly classified as follows: heaps, stalls, cylindrical furnaces with superimposed hearths, blast-roasting apparatus. These methods will be found described at length in Section X.

**Types of Smelting Furnaces.**—Two types of furnace are employed in the smelting of copper ores, the blast furnace and the reverberatory furnace. In the blast furnace the ore and fuel are in intimate contact, the fuel being burned by means of a blast of air forced through the interstices of the column of ore and fuel. Coke is generally employed as the fuel, though of late years pulverized coal has been used to some extent.

In the reverberatory furnace, the fuel and ore are not in intimate contact, and the products of combustion of the fuel pass over the ore charge and are guided in their course by a more or less horizontal roof. The fuel used in the reverberatory furnace may be coal, pulverized coal, oil, or gas.

The blast furnace is used mainly for the treatment of coarse ores over 1 in. in diameter, though in many cases much finer ore than this is treated successfully. The reverberatory furnace is almost universally used for the treatment of fine ores, such as table concentrates, flotation concentrates, flue dusts, etc., though the development of the modern reverberatory has progressed to the point where it has often been found to be more economical to crush the coarser ore to  $\frac{1}{4}$  in. and treat in the reverberatory rather than in the blast furnace.

The early types of blast furnace were constructed of brick and the molten products were collected in a crucible located at the lowest point of the furnace. This type of furnace had two great disadvantages in addition to its small capacity. These were the destruction of the shaft at the smelting zone, and the impossibility of making a clean separation between the slag and the matte.

The first of these difficulties was overcome by the adoption of the water jacket, which not only eliminated the corrosion, but also permitted a higher temperature to be carried, resulting in a more fluid slag. The second difficulty was solved by the use of the external settler, which not only gave an efficient separation between the slag and matte, but also allowed the speed of the furnace to be greatly increased.

The modern blast furnace consists essentially of a long, narrow, water-jacketed shaft. The dimensions, particularly the length, vary considerably, being proportioned to the capacity of the furnace. The size of furnaces is expressed in terms of the dimensions at the tuyère level. The width, being limited by the ability of the blast to penetrate the charge, is generally from 44 to 48 in., though some furnaces are as narrow as 30 in., and others as wide as 56 in. As the width is practically fixed within narrow limits, the only manner in which capacity may be obtained is by increasing the length, and present-day furnaces have lengths of 180 in. to as much as 1,044 in., in the case of the huge Anaconda furnaces. The capacity of blast furnaces depends greatly upon local conditions but may be said to vary from 4.5 to 9.0 tons per square foot of hearth area per day. The bottom plate of the furnace is generally a heavy, ribbed, cast-iron plate, supported by jackscrews. Upon this is laid a layer of fire-brick, though special circumstances may require the use of silica or chrome brick. Resting on the bottom plate are heavy cast-iron plates bolted together, forming the walls of the crucible. These are generally heavily ribbed to insure the necessary strength and are lined with the same material as is used on the bottom. In some instances, the walls of the crucible are formed by a set of water jackets, but the usual practice is to have the lower tier of water jackets rest directly upon the bottom plate, the lower ends being below the level of the matte and slag to prevent their burning through in case sediment collects in the water space.

When the blast furnace is started, the radiation from the bottom and through the water jackets forms a crust of chilled material which remains permanently. This crust adjusts itself to the operations of the furnace. If it wears down, the increased radiation soon restores it to the proper thickness, while if the furnace cools down the radiation is decreased, the bottom builds up, and, when the furnace is once more at proper heat, the additional thickness is soon melted off.

The water jackets are generally in two tiers. The lower jackets rest either on the crucible plates, or, as has been stated, directly on the bottom plate. The upper tiers are suspended from I-beams which carry the furnace superstructure. The upper jackets rest on the top of the lower jackets. The lower side jackets are given a slope towards each other to form a bosh, the upper and end jackets being vertical. The amount of bosh depends upon the amount of reducing action desired, as the greater

the amount of bosh the greater will be the reducing action. The water jackets are constructed of flanged steel plate, the inner side being  $5\frac{1}{8}$  to  $3\frac{1}{8}$  in. thick, the outer side being somewhat thinner,  $\frac{1}{4}$  to  $5\frac{1}{16}$  in. The water space between the sides of the jacket varies from 3 to 5 in. The jackets are stiffened by means of angle iron running vertically in the water space. Each jacket has its individual feed and discharge pipes for the cooling water, and where water is plentiful each jacket may be on a separate circulation, but where water is scarce the outlet of the lower jackets may be fed to the upper jackets.

The lower side jackets are pierced for the tuyère openings, there being usually three tuyères to each jacket. The opening is usually 4 to 6 in. and a steel thimble having a slight taper is welded to the inner plate and riveted to the outer plate. The tuyère pipes are generally of cast iron, and are bolted securely against the jackets, any leakage being prevented by asbestos packing. There is usually a cap on the outer end of each tuyère pipe, which is readily removable to permit of punching the tuyères when necessary.

The tuyère pipes are connected by short branches to the main bustle pipe which carries the main air supply, the amount of blast to each tuyère being regulated by means of a valve. The volume of air required by the furnace varies widely, published figures being 190 to 400 cu. ft. per minute per square foot of hearth area at a pressure of 32 to 40 oz. It is probable that the variation in these figures is due to their being derived by taking the revolutions per minute of the blowers or the piston displacement, neither of which are accurate due to the great amount of leakage.

The breast jacket is located either in the side or the end of the furnace, the location being largely determined by the available floor space and the general arrangement of the plant. It contains the opening for the removal of the molten products of the furnace and is securely attached to the adjoining jackets. The slag spout conveying the slag and matte from the furnace to the settler is fastened to the breast jacket in such a manner as to permit of its ready removal when required with minimum delay to the furnace operations. The spout may be constructed of wrought iron, steel, copper, or bronze, and is water cooled. The blast is trapped by having the discharge end of the spout about 18 in. above the opening in the breast jacket, so that as the molten material from the furnace rises in the spout there is sufficient head to overcome the pressure of the blast. The shape of the slag spout depends upon the fancies of the designer of the furnace, there being many different designs in use, all of which appear to be giving satisfaction.

The jackets generally carry the shaft of the furnace to the level of the charging floor, though in some instances they are surmounted by several courses of fire brick. Just below the charging floor there is generally a set of feed or apron plates for the purpose of distributing the charge uniformly in the furnace by directing the fine material towards the center of the shaft while permitting the coarse material to fall along the sides. In many furnaces, however, these plates are omitted owing to local conditions making their use unnecessary.

Above the level of the charging floor is the superstructure of the furnace with the arrangements for feeding the materials of the charge and the removal of the furnace gases. There are many modifications in the design of the superstructure. In many cases it is of brick to a height of 12 to 14 ft. surmounted by a steel hood for the removal of the gases. In other plants the entire superstructure is of steel and occasionally water jacketed.

The general practice of charging is through openings in the sides of the superstructure, which may or may not be kept closed by doors between charging. With the development of mechanical charging devices the gases are in some instances drawn off below the point of charging, particularly where the gases are utilized in the manufacture of acid. Care should be taken to keep the charge openings closed between charges

on account of the great leakage of air that would otherwise occur, with its consequent detrimental effect upon the draft of the furnace.

Air- or water-cooled steel hoods have marked advantages over the brick hood on account of the ready removal of accretions therefrom, and there seems to be less tendency for these accretions to form on this type of hood.

The furnace gases, on leaving the hood, pass through a downcomer of brick or steel, then to some sort of a settling chamber to remove the coarse particles of dust, and thence to the stack. The recovery of the flue dust is a matter of serious importance and the methods used will be discussed at a later point.

The settler serves not only as a means for separating the slag and matte by reason of the difference in their specific gravities, but also as a reservoir for the storage of matte until such time as it may be required. A plant which treats its own matte, therefore, requires a larger settler than does one that casts its matte directly into molds for shipment to some other plant for treatment. The settler is circular or oval, depending on local conditions and the plant layout, and consists of an iron shell lined with refractory material. The diameter may be as great as 26 ft. though 18 ft. is the usual dimension, the depth being 4 to 5 ft. The lining material varies greatly and depends upon the grade of the matte, and character of the slag, the most rapid wear being occasioned by the very corrosive and fiery low-grade mattes usually accompanied by basic slags. A high-grade matte and an acid slag seldom cause much trouble through corrosion. The settler lining, where there is little corrosion, may be made of fire brick or silica brick; where corrosion is feared, the lining is generally of magnesite or chrome brick, or a combination of the two. Frequently chromite or chrome ore is rammed into place and faced with a row of bricks to hold it in place until the heat of the molten material sinters it together. The lining is frequently protected by spraying water on the steel shell of the settler; this keeps the outside cool and causes a crust to form on the lining.

The roof of the settler is formed by the chilling of the slag, amounting to a thickness of several inches except at the point where the molten stream enters and leaves. The working platform was formerly this chilled crust but is at the present time a steel platform directly over the settler.

The slag overflows are constructed of cast iron coated with clay or other material, and are situated as far away from the entrance as possible, thus affording more time for settling. In many cases these overflows are situated at the side of the settler, due to the arrangement of the plant. The slag quietly flows out of the settler and through these overflows into slag cars by which it is conveyed to the dump, or else it may be granulated by means of a strong stream of water, which not only granulates it but also carries it through launders to the dump.

The matte is withdrawn from the settler through tap holes situated close to the bottom. There are generally two of these holes, though many plants have but one. The hole in the wall of the settler is  $1\frac{1}{2}$  to 2 in. in width and may be lined with chrome brick. Opposite this opening and attached to the shell of the settler is a copper or iron frame in which is securely wedged the tapping plate, which may be either iron or copper. The tapping plate has a 1-in. hole in the center into which a clay plug is rammed. A steel tapping bar is rammed through the clay plug until it almost reaches the matte and remains in that position until the tap is made. This is accomplished by withdrawing the steel bar by sledging against wedges held in place on the bar by rings. The matte flows from the tap hole into the matte launder of cast iron, thickly coated with clay to protect it from corrosion, and from thence into the ladle, which is usually of steel lined with cement and clay. During the tapping the workers are protected from the heat and splashes of matte by means of a slotted sheet-iron door which is swung out of the way when not required.

The charging of the blast furnace is accomplished in a number of ways. Hand charging gives the best regulation of coarse and fines and also possibly effects a saving of coke. It is frequently used up to capacities of from 300 to 350 tons per day and in some cases even higher. It, however, is expensive and too slow for the average modern blast furnace smelting 600 to 700 tons per day, and has, therefore, been superseded by some form of mechanical charging, particularly as the larger furnaces are less sensitive to slight irregularities in the charges than the smaller furnaces.

The general plan in use at the present time is to charge the furnace from side dump cars, varying greatly in their design, which are brought to the furnace in a train by a locomotive, and travel on tracks on each side of the superstructure. The contents of the car may be dumped at one point or the car may be moved along the length of the furnace while being dumped in order to distribute the charge.

Another scheme provides for the charges being brought to the furnace in cars and dumped on the charging floor from which they are pushed into the furnace by a mechanical pusher. At Granby, the furnaces are charged by pushing the charge cars into the furnace at the ends, from which they run on tracks inside the furnace to the point of discharge. This gives a straight fall of material and provides good distribution.

In some plants the coke used for fuel is mixed with the charge and then sent to the furnace, but the usual practice is to charge it separately, and the utmost endeavor is made to keep the consumption of coke at a minimum, although this is not always easy to do, as the average furnace man considers coke as a panacea for all ills.

Sizes of modern blast furnaces are shown in the following table:

	Area, inches	Blast, ounces	Capacity, tons
United Verde.....	48 by 320	40	950
United Verde Extension.....	48 by 312	30	600
Mason Valley.....	66 by 420	33	1,000
Calumet and Arizona.....	48 by 480	35	900
Garfield.....	48 by 240	40	600
Tacoma.....	45 by 261	35	650
Anaconda.....	56 by 612	40	1,400
Anaconda.....	56 by 1,044	40	2,500

The modern furnaces are vastly more efficient and economical than those formerly in use. Due to the large amount of material in the furnace, they are less susceptible to slight irregularities. There is a saving of fuel, possibly amounting to 10 per cent, and there results a higher furnace temperature, giving hotter slag and enabling a more siliceous charge to be run. There is a marked decrease of incrustations, which eliminates the necessity for much barring. It has been found possible to change a leaking jacket without shutting the furnace down. This is accomplished by blocking off the tuyères in the leaking jacket as well as those in the adjacent jackets and allowing a crust to form which is sufficiently strong to support the charge during the short period necessary to make the change.

There are three distinct processes in blast-furnace smelting: (1) The reduction process, in which a considerable percentage of coke, 15 per cent, is used. The blast oxidizes the carbon of the coke and but little of the sulphur in the ore. This is the process most generally used. (2) The pyritic process, in which raw, massive sulphides

are smelted in a highly oxidizing atmosphere without the addition of carbonaceous fuel. The heat generated by the oxidation of the sulphur and iron is sufficient to maintain a continuous operation. (3) The partial- or semipyrritic process in which sufficient heat is not generated by the oxidation of the sulphides and carbonaceous fuel is added to the charge in just sufficient quantity to overcome the deficiency.

**The Reduction Process.**—This process is characterized by the use of carbonaceous fuel as the principal source of heat. The sulphur content of the charge is sufficient to form the desired matte, and any oxidation is generally undesirable. The percentage of coke, which is the usual fuel used, varies from 12 to 15 per cent. An excessive amount of coke is liable to cause a reduction of iron from the slag, while with a shortage the furnace becomes chilled and suffers a loss of tonnage.

The use of such an amount of coke means that the furnace always contains a large mass of glowing coke for a considerable distance above the tuyères, and consequently the oxygen in the blast is consumed almost immediately, resulting in a strong reducing atmosphere. Such being the case, it is readily seen that any sulphides present will melt down unchanged and form matte. An ore high in sulphur would, therefore, yield a large amount of matte which is expensive to treat, and it is clear that little would be gained by the reducing smelting of such an ore, and that a portion of the sulphur must be eliminated by a roasting process previous to the treatment in the blast furnace, or else the sulphides may be mixed with oxide copper ores to increase the grade of the matte. A certain oxidation of sulphur may be accomplished in the blast furnace by keeping the ore column low and increasing the blast, but such procedure generally results in a very hot top and high temperatures of the waste gases, and in general is not economical.

Regarding the chemistry of the process, the blast entering through the tuyères oxidizes the carbon of the coke to  $\text{CO}_2$ , which is then partly reduced to  $\text{CO}$  by the glowing mass of coke in the furnace, the resulting gases being a mixture of  $\text{CO}$ ,  $\text{CO}_2$ , and the nitrogen of the air. As these gases rise in the furnace and reduce the oxidized materials, the percentage of  $\text{CO}_2$  increases and will predominate in the waste gases. Any remaining  $\text{CO}$  is usually burned to  $\text{CO}_2$  in the upper part of the furnace.

As the charge descends in the furnace, its moisture is driven off almost immediately, followed by the decomposition of such carbonates as may be present. At a lower point the oxides and silicates of copper will be reduced, and on coming into contact with metallic sulphides will be converted into copper sulphides which, with any existing sulphides, melt and flow downwards to the crucible collecting the silver and gold as they descend. Ferric oxide ( $\text{Fe}_2\text{O}_3$ ), is reduced to ferrous oxide ( $\text{FeO}$ ), which combines with the silica to form slag as does any lime or other flux added to the charge. When the molten materials have collected in the crucible below the tuyères the various sulphides adjust themselves to form the proper matte, and likewise the various slag components adjust themselves to form the proper slag.

**The Pyritic Process.**—The feature of this type of smelting is that the heat necessary to conduct the operation is furnished by the oxidation of the constituents of the ore, little or no extraneous fuel being used for this purpose. Up to 2 to 3 per cent of coke may be added to the charge purely as a preheating medium and possibly to secure a more open charge. It certainly never reaches the smelting zone.

The essential requirements for pyritic smelting are siliceous material, which is high in free silica, and heavy pyrite ore. It is necessary for as much of the silica as possible to be in the free state in order that it may combine with the ferrous oxide at the instant of its formation. Combined silica is unsuited to the pyritic process as it

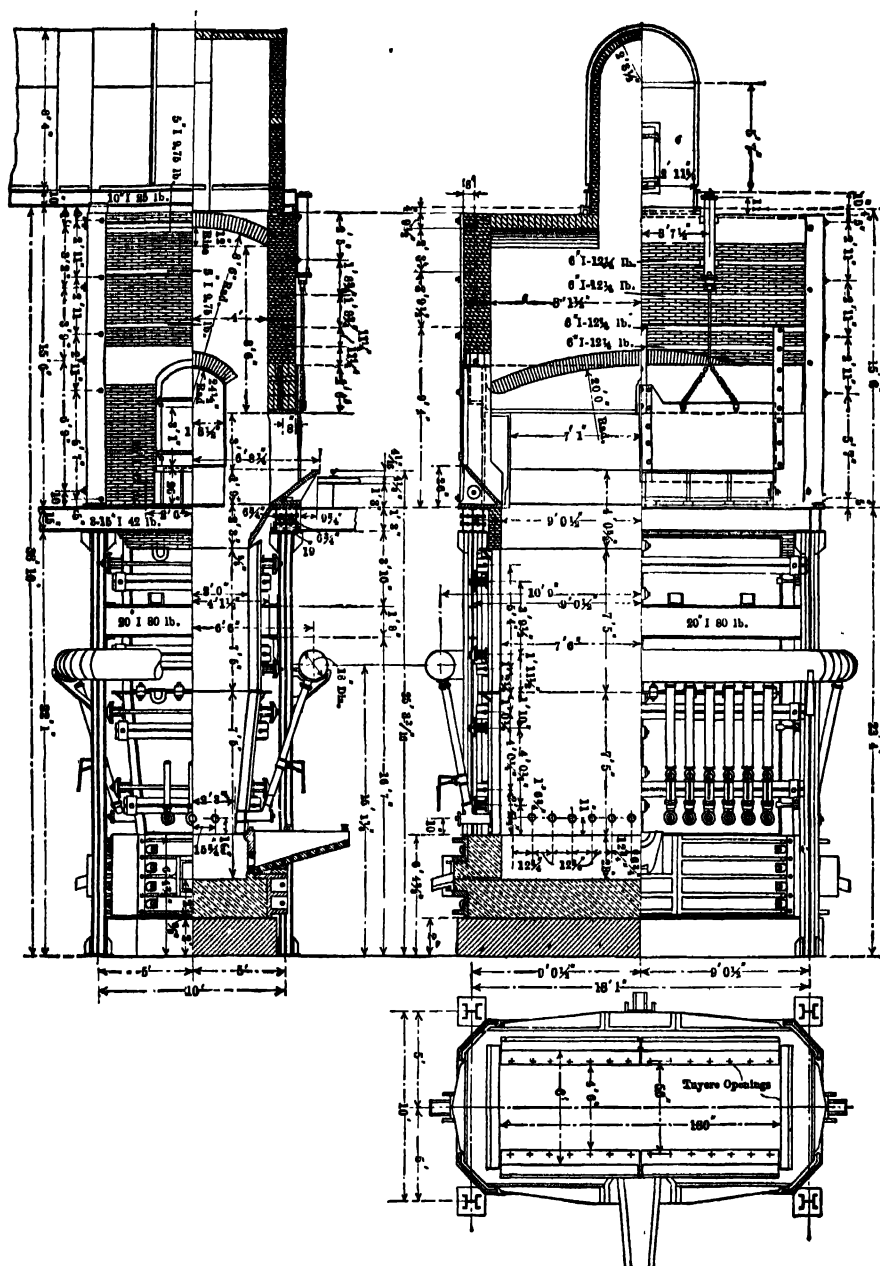


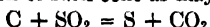
FIG. 1.—Typical copper-blast furnace.

is already united with one or more bases and consequently requires a large amount of heat to break up the existing combinations and form new ones with the ferrous oxide, and generally in the pyritic process there is not any too large a margin of heat.

The pyrite ore not only furnishes the heat for the operation, but also the sulphur for the matte required, and it must consist largely of iron pyrites, as any oxidation of the copper sulphides would result in the slagging and consequent loss of the copper oxide.

As the charge sinks in the furnace, any moisture present is quickly driven off, followed by the dissociation of the limestone added as flux. The free sulphur in the sulphides will be expelled as heavy fumes of elemental sulphur, and at a point just above the smelting zone the pyrite has been changed to  $\text{FeFeS}$ , which is the true pyritic fuel of the process.

The blast entering the furnace through the tuyères strikes the hot fused sulphides, oxidizing the Fe to  $\text{FeO}$  and the S to  $\text{SO}_2$ . The  $\text{FeO}$  simultaneously unites with the silica to form a ferrous silicate slag, while the  $\text{SO}_2$  rises through the charge and preheats it assisted by the oxidation of such coke as may be present:



The matte collects below the tuyères, as does also the ferrous silicate slag after uniting with the lime to form the final slag. The fused mixture then flows through the spout to the settler.

The grade of the matte produced and the acidity of the slag are controlled by the volume of air blown into the furnace. A reduction in the amount of air will cause less of the sulphide to become oxidized, and the grade of the matte will, therefore, be lowered. At the same time the slag will become more siliceous, as less iron is oxidized, and this condition will interfere with the process unless the amount of siliceous material in the charge be reduced. On the other hand, any increase in the volume of air will oxidize an additional amount of iron, raising the grade of the matte and increasing the iron in the slag unless additional silica is provided.

A peculiarity of the pyritic process is the artificial bosh formed on the side and end walls of the furnace. This contracts the smelting area to a long, narrow slit. This bosh is composed of fragments of quartz stuck together by slag or by superficial softening, and seldom contains matte. Its position in the furnace is not fixed, but varies under different conditions.

While in reducing smelting the tuyères are bright, in pyritic smelting they are dark and are bridged across. It has been stated that a bar can be passed through the furnace from one tuyère to the opposite tuyère and be cool when withdrawn. This indicates that the zone of fusion is well above the tuyère line, and that the molten material passes through channels between the tuyères.

Partial pyritic smelting is used when the available sulphide ores are not massive but consist of pyritic material disseminated throughout the gangue, which is generally low in free silica and which may contain some alumina. Such ores are not capable of furnishing by themselves sufficient heat for the continuance of the process, and it is, therefore, necessary to add carbonaceous fuel. In some instances it has been found advantageous to preheat the blast, as thereby a saving is accomplished in the amount of fuel used.

In the partial pyritic process the slags are rather low in iron, as the presence of coke requires much of the oxygen of the blast for its combustion, and there is less available for oxidizing the iron in the sulphides. The excess silica will, therefore, have to be taken care of by the use of lime. In order that there may be any considerable pyritic effect, a large amount of blast is necessary and this usually results in the furnace having a hot top.



The smelting zone is nearer the tuyère level and is not so contracted as in pyritic smelting, but is higher and more contracted than in reducing smelting. The tuyères are frequently dark and require a great deal of punching to keep them open.

The principal features of the blast furnace for the treatment of coarse ores are that its construction is simple and the erection is comparatively inexpensive. Where small installations are required they can be purchased complete and are easily transportable from one location to another. The furnace is easily started and shut down, and the operation is relatively cheap. The fuel consumption is low and there is the possibility of utilizing the fuel value of the iron and sulphur in the charge, and the heat is efficiently communicated to the individual parts of the charge.

The blast furnace is exceedingly elastic in its operation, and changes in the ore supply are readily handled with little trouble. It is capable of handling practically every class of copper-bearing material in lump form, and, with modern sintering facilities, much fine material can also be treated that would otherwise be uneconomical to handle.

**The reverberatory furnace** is used for the treatment of fine ores, and the fuel and ore are kept separate, the former being burned in a separate compartment from which the flame and hot gases pass over the ore, being guided in their course by a more or less horizontal roof. The heating of the ore is accomplished by the radiation from the roof and side walls rather than by direct contact with the hot gases.

It is particularly suitable for fine materials on account of the relatively quiet atmosphere due to there being no blast, and there are greater opportunities for the settlement of dust than in the blast furnace. As the furnace atmosphere is neutral, or very nearly so, it has little or no influence on such reactions as occur in the furnace, and it, therefore, follows that the reverberatory is purely a melting furnace.

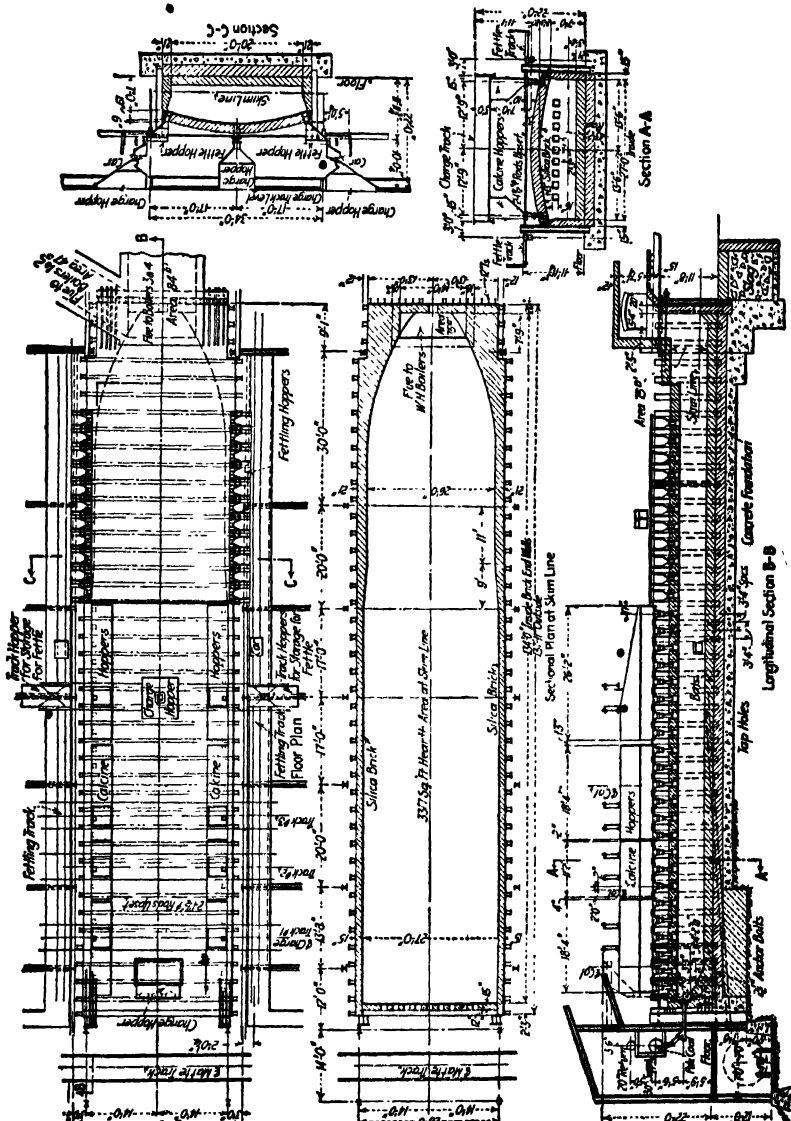
The functions of the furnace are that it shall melt down ore and flux as rapidly as possible with a minimum of heat loss; it should permit the formation of matte and slag from the mixture of oxides, sulphides, and sulphates in the charge; and the temperature must be sufficiently high to render the matte and slag perfectly fluid in order that there may be complete settling with a minimum of loss in the slag.

In order that the furnace may melt as rapidly as possible, it is necessary that there be a good draft, in order that the great volume of gases which have been cooled down by their contact with the roof, walls, and charge be replaced as speedily as possible by fresh, hot gases. Unless this condition is present, there will result a serious reduction in the tonnage that the furnace will handle.

In order to provide the required heat for the melting, it is necessary that fuel be burned as fast as possible. With grate firing, this requires large grate area, as thereby there results less cooling of the furnace by the frequent additions of fuel, a higher calorific intensity due to large amounts of fuel being burned at one time, and a better combustion. When pulverized coal or oil is used, sufficient burner capacity must be used to produce the required number of heat units per minute.

The heat losses are kept at a minimum by the elimination of side-door charging with its consequent admission of large volumes of cold air; the walls and roof are made as thick as economically possible to reduce the radiation losses; a deep bath of molten material is kept on the hearth continuously instead of tapping the entire contents of the furnace and recharging with cold material as in the early methods of operating. These cold charges of the early smelters required a very large part of the furnace time to heat up and bring to the point of fusion, the actual operation of smelting occupying but a small proportion of the time. The cold material formed a blanket on the top

of the charge through which the heat penetrated with difficulty, and it was necessary to stir the semifused mass frequently in order to prevent it from sticking to the bottom. In the present method the bath of molten material is highly superheated and readily gives up its heat to the fresh charges which are made frequently and in small amounts.



**Fig. 2.—Reverberatory smelting furnace at Nevada Consolidated smelter.**

The heat of the gases is utilized to the greatest possible extent by making the furnace as long as will permit the charge being kept in a fluid condition without an excessive consumption of fuel, and such heat as necessarily leaves the furnace as sensible

heat in the waste gases is, to a large extent, recovered by passing them through waste-heat boilers.

The hearth is of silica sand 24 to 30 in. in thickness. The sand is given a preliminary calcining and is then leveled and sintered into place by long, continuous firing. As the modern practice is not to drop the charge on the hearth, but on a bath of molten material which is supported by the hearth, there is little wear on the latter, resulting in a very long life.

The length of the hearth depends upon the capacity desired. As the width of the roof is limited by constructional details, capacity, therefore, depends upon the length, and in the most recent furnaces this has reached the enormous figures of 120 to 130 ft. The old practice of having a vault under the hearth was abandoned on account of the great loss of heat through the hearth which seriously interfered with the rapidity of the smelting operations, and all modern furnaces have solid bottoms.

The side walls of the furnace are constructed of silica or magnesite brick and are thicker below the slag line than above to better withstand the additional pressure. The roof of the furnace is universally constructed of silica brick 15-20 in. in thickness, and constructional problems limit the width to 28-30 ft.

The entire furnace is heavily ironed and stayed for resisting the thrust of the hearth and roof, a modern installation having 20-in. I-beams spaced on 5-ft. centers, the bottoms held in place by concrete abutments, the top of the buckstays being held by heavy tie rods.

Modern practice demands that the reverberatory charge be preheated. As the fine ores which form the bulk of the charge usually have to be roasted, particular effort is made to deliver the resulting calcine at the highest possible temperature. The flux is frequently added to the roasters in order that it may be charged at the same temperature as the remainder of the charge. The charge is introduced into the furnace through charge holes in the roof. These are frequently water cooled and are usually located along the side walls for about half the length of the furnace. The object of charging along the side walls is to keep them covered with the charge and thus protect them from the action of the hot gases. The usual charge is about 10 to 15 tons at one time and as this is introduced into the furnace it floats and spreads out on the bath of molten material on the hearth. The highly superheated bath readily gives up heat to the fresh charge and it receives further heat from the radiation from the roof and quickly melts.

The resulting slag and matte now move towards the tapping end of the furnace and have ample time in which to separate cleanly. The slag may be tapped intermittently or allowed to flow off continuously, the latter coming more into favor as it results in cleaner slags. The matte is tapped from the fore part of the furnace, as required by the demands of the converters in a manner similar to tapping a blast-furnace settler.

The fuel used in the modern large reverberatory furnace is pulverized coal or fuel oil, depending upon the relative cheapness of the two fuels. When pulverized coal is used, it is ground so that 80 to 90 per cent will pass a 200-mesh screen, and is blown into the furnace with about 15-oz. air pressure. The coal used may vary in ash content from 6 to 7 per cent up to as high as 15 to 20 per cent without giving trouble. The ratio of charge to fuel varies from 5 to 7½. The burners are inserted directly in the rear wall of the furnace and several burners are used, four to six being the usual number. The type of burner varies in each plant with apparently equally satisfactory results.

When using fuel oil in the furnaces it is generally 17 to 19 Bé. and is preheated to about 200 to 250°F. before burning, as this results in fuel economy. The amount of fuel oil used per ton of charge varies from 0.50 to 0.70 bbl. When as much heat as possible has been extracted from the gases, they are passed through waste-heat boilers

for a further recovery. These are 500 to 750 b.h.p. and they frequently are connected to a common cross flue extending from all the reverberatory furnaces, so that in case of a shutdown of a furnace the boiler capacity will not be lost, and if a boiler is down for cleaning or repair the other boilers are available for the utilization of the waste heat. It has been found to be advisable to have the flues from the furnaces to the boilers slope slightly towards the furnaces, as otherwise trouble may be experienced from the accumulation of slag.

In the reverberatory furnace any reducing action is performed by the sulphur in the charge. This reacts with the oxides and sulphates to produce metallic copper and sulphur dioxide. The metallic copper is then sulphurized by the sulphides of iron present, oxidizing the iron to  $\text{FeO}$ , which combines with the silica present to form the slag. The reverberatory furnace will make a higher silica slag than a blast furnace, due to the higher available temperature. Any iron oxide ( $\text{Fe}_2\text{O}_3$ ) present in the charge is acted upon by the sulphides and reduced to  $\text{FeO}$ , uniting with the silica.

The grade of matte produced by the reverberatory furnace depends upon the degree of roasting that the ore has received. If a higher grade of matte is desired, the roast is carried to a higher degree, and if the matte is too high, the roast is not pushed to the same completeness. In the roasting, care must be taken that no magnetic oxide of iron ( $\text{Fe}_3\text{O}_4$ ) is formed, as such material forms a mush in the furnace and is difficult to remove. When it occurs the remedy is to add a large amount of green sulphide ore to the charge, which will reduce the magnetite to  $\text{FeO}$ .

Comparing blast-furnace and reverberatory-furnace smelting, the former requires coarse ore in order to give the best satisfaction, little space is required, and the investment is low for any given tonnage. The fuel, though small in amount, is relatively expensive, and considerable power and a large amount of cooling water are required. Blast-furnace slags can be made between very wide limits, but the addition of a large amount of flux results in the production of a large amount of slag with a corresponding metal loss.

The reverberatory furnace is the most satisfactory and advantageous apparatus in which to treat fine ores, but it usually requires an extensive roasting plant and in itself occupies a large amount of space and locks up a large amount of valuable metal. Hence the investment is large for a given tonnage. While large amounts of low-priced fuel are used, a large proportion of the heat in the gases is recovered in waste-heat boilers and this greatly reduces the power cost. The amount of slag, and, consequently, the metal loss, are less than with the blast furnace. With the ever-increasing amount of fine ores to be treated the reverberatory furnace is fast displacing the blast furnace and it has been found advantageous in certain localities to use reverberatory smelting for coarse ores that under ordinary conditions would go to the blast furnace.

**Converting.**—When copper and other valuable constituents of the ore have been concentrated into the matte, and the worthless material disposed of as slag, the next step in the process is the removal by oxidation of the iron and sulphur of the matte. This is accomplished by transferring the molten matte to a refractory lined vessel, known as a converter, and forcing thin streams of air through the liquid mass. The reactions involve the rapid oxidation of the iron and sulphur and the fluxing by silica of the iron oxide thus produced. The sulphur dioxide formed by these reactions passes off in the waste gases. The heat of oxidation is such that the materials are kept in a molten condition and the temperature is maintained well above that necessary for the formation of the slag, so that the process is independent of heat from external sources. The copper, together with any silver or gold, is reduced to the metallic form, and is cast into suitable shapes for transportation to the refinery for further treatment.

The converter is a cylindrical iron or steel vessel lined with refractory material. A conical mouth is provided through which the matte is introduced, the slag and blister copper withdrawn, and the gases pass to the stack. The air for the oxidation is introduced through the side of the converter by means of tuyères leading from an wind box attached to the outside and having a connection with the blast main.

The early types of converters were blown from the bottom, similar to those used in the steel industry, but this method was not a success, due to the chilling effect of the blast on the copper, which, when produced, sank to the bottom of the converter and froze in the tuyères, thus stopping the operation. This was remedied by raising the tuyères so that there was space for the copper to settle underneath the blast.

Converters are classed as upright or horizontal, depending upon the direction of the long axis of the cylinder, and are so mounted that they can swing in a vertical plane for the purpose of receiving or withdrawing the molten materials. The upright type of converter has the advantages that, owing to the greater depth of matte, the oxidation is more rapidly conducted, the lining is more efficiently supported, and the wear is found to be less in amount and more uniformly distributed. The greater depth of matte, however, necessitates a greater blast pressure, and the operations are more difficult of control than in the horizontal type.

The horizontal type takes the same amount of matte in a less depth, thereby requiring a smaller blast pressure, the converter can be tilted in order to regulate the depth over the tuyères, and the operation is easier to control.

The refractory lining may be composed of either acid or basic material. The acid lining, though formerly universal, is practically entirely supplanted by the basic lining. The functions of the lining are to preserve the steel shell and form a receptacle for the molten materials, and to prevent radiation losses to the greatest possible extent.

In the acid lining the material used should contain the largest possible amount of free silica. The material generally used is low-grade siliceous ore, which, while it may not be as desirable metallurgically as quartz, is smelted for nothing, and the values recovered from an otherwise profitless material make the substitution economical. The ore is crushed and mixed with a binding material in a mill, and is pounded down hard in the bottom of the converter by tamping machines until it reaches to the proper distance below the tuyère level. At this point a steel or wooden form is placed in the converter and the lining material is rammed around the form in layers about 6 in. in thickness. When the operation is completed the form, which is sectional, is removed and the tuyère holes are punched in the lining. The hood is then inverted and lined and placed upon the body of the converter and securely bolted in place, the joint being covered with clay.

The freshly lined converter is now dried slowly by a wood fire, after which coke is added and kept burning by an air blast through the tuyères for 5 or 6 hr., after which the converter is ready for operation.

The basic lining is almost universally magnesite brick, the thickness varying from 9 in. at the top and sides to 18 in. along the tuyère line and bottom. The brick may be laid in magnesite powder and linseed oil, or sodium silicate may be substituted for the linseed oil. In order to furnish room for proper expansion liners consisting of thin strips of wood are placed at intervals along the sides. After lining the shell, it is carefully warmed to prevent spalling and is then ready to be placed in the stand.

The air for oxidizing the sulphur and iron is admitted through tuyères usually 1 in. to 1½ in. in diameter, placed about 8 to 12 in. above the bottom. The tuyères are connected to an wind box having openings opposite each tuyère to permit of punching when necessary. These openings are provided with ball valves to prevent leakage of air while the converter is operating. The air is supplied at a pressure of 10 to 20 lb., depending upon the type of converter used and the depth of matte carried.

The amount of air required will depend, of course, upon the grade of matte being converted, but will average 160,000 to 200,000 cu. ft. of free air per ton of blister produced for a 40-per cent matte.

The grade of matte which is most economical to treat in the converter depends upon the cost of the preceding operations. A low-grade matte, low in copper but high in iron, has the advantage of enabling a high temperature to be obtained due to the fuel value of the FeS. On the other hand, the amount of iron that must be slagged requires a corresponding amount of silica, and produces a large amount of slag carrying considerable copper which is too valuable to waste, and must, therefore, be retreated for the recovery of the copper contents. The amount of copper per ton when using low-grade matte is relatively small, and the cost of treatment therefore high.

A high-grade matte, high in copper but low in iron, has the disadvantage of containing less heat, and there may be difficulty in maintaining the desired temperature. The amount of slag produced is decreased with a consequent lower retreatment cost per ton of copper produced, and the cost of converting is reduced due to the larger amount of copper per ton of matte. The economical grade is reached, other things being equal, when the cost of fluxing the iron in the regular smelting operations is less than doing so in the converter.

The operation of acid converting is conducted by first heating the converter to the required temperature by the use of wood and coke. The proper amount of matte is then introduced through the mouth, the blast turned on, and the converter turned up so that the mouth is under the hood conveying the gases to the stack. The tuyères are now below the surface of the matte and the oxidation commences. There are two main stages in the operation: first, the elimination of the iron, or blowing to white metal; and, second, the elimination of the remaining sulphur, or blowing to blister.

During the first stage the iron sulphide is oxidized to FeO, the sulphur oxidizing to SO<sub>2</sub> and passing off in the waste gases. The FeO immediately attacks the siliceous lining to form the slag. Any copper that may be oxidized is immediately resulphurized by reacting with the iron sulphide. As the oxidation proceeds and the iron is slagged, the matte remaining in the converter gradually approaches white metal (Cu<sub>2</sub>S). This change may be followed by noting the character of the flame issuing from the mouth of the converter. At the start of the operation it has a reddish color changing to a green, and as the white-metal stage approaches, to a pale blue. If, however, an impure matte is being converted the flame indications are unreliable, and dependence is placed upon the appearance of the layer of matte upon the punch rod which is inserted in the tuyères to keep them open for the passage of the blast. When the white-metal stage has been reached, it is indicated by the working of the matte on the rod.

When the iron has been slagged, the converter is turned down, the blast shut off, and the slag skimmed into a ladle. In order to determine when the slag has been skimmed clean, a rabble is held under the stream and any white metal coming over will be seen by its working on the iron of the rabble. When the slag has been skimmed, a fresh charge of matte may be introduced and the operation repeated. This is known as doubling, and is done for several reasons. If the temperature of the charge is too low, there may be danger of freezing during the finishing blow; the fresh addition of matte, therefore, gives fresh fuel with which to raise the temperature. If the matte is low grade, there may not be sufficient white metal present to cover the tuyères and, therefore, more matte must be added. If the converter cavity has become enlarged, the same condition prevails, and sufficient matte is added until the amount of white metal remaining is sufficient.

During the second stage the sulphur in the white metal is oxidized, the sulphur passing off in the gases as sulphur dioxide, the oxidized copper reacting with the

remaining white metal to produce metallic copper and sulphur dioxide. The copper settles below the tuyère level and collects any silver and gold that may have been in the matte. During this period the flame of the converter changes from a pale blue to reddish brown, and the metal on the punch rod becomes more and more coppery. When the charge is finished, the converter is turned down, the blast shut off, and the metallic copper poured into a ladle for casting, or it may be cast direct from the converter. The former practice is to be preferred, as the latter causes too much delay to the converter and keeps down the tonnage treated per day.

The main objection to the acid process of converting is the rapid destruction of the lining by the union of the  $\text{FeO}$  with the silica, the latter being the sole source of silica supply. The life of an acid lining is limited to a relatively few charges, depending upon the grade of matte converted, a low-grade matte being more destructive than one of higher grade, due to the larger amount of iron slagged. The expense of constantly renewing the lining was heavy and for years efforts were made to find a lining that would not be attacked by the iron. After many attempts and failures this was successfully accomplished by Peirce and Smith.

**Basic-lined Converters.**—The operation of converting in the basic-lined converter is similar to the acid operation as far as the reactions go, but the silica for slagging must be supplied from some external source. As the charge of matte is in the converter, the necessary amount of siliceous ore is added, the blast turned on, and the converter turned up. The flux is generally thoroughly dried before being added to the matte to avoid explosions, though in some plants the siliceous flux is blown into the converter and spreads out over the matte in thin layers and, consequently, does not have to be dried.

The basic-lined converter cannot be operated at the temperature of the acid converter on account of the destruction of the magnesite lining at high temperatures. The lower temperature required necessitates a great deal of punching of the tuyères. With a low-grade matte there is a greater heat liberation than when a high-grade matte is being converted, and great care is necessary that the bath be not overheated. Too high a temperature retards the converting, attacks the lining, and tends to warp the converter shell. On the other hand, too low a temperature makes the tuyère punching very difficult, makes a sticky slag, and is liable to cause the formation of magnetic oxide of iron which builds up on the bottom and sides of the converter. Due to the nature of the process, the basic converter operates at a lower temperature than the acid process, mainly on account of the large quantities of cold ore added as flux.

The critical stage of the operation is at the finish of the slagging period. If there is insufficient silica present to take care of the iron, magnetite will be formed, while an excess of silica causes a sticky slag. Magnetite is also caused by an insufficiency of silica during the blow to white metal, and this has been taken advantage of to give added protection to the lining. Wheeler and Krejci at Great Falls, Mont., patented a process of blowing a low-grade matte with either no silica or else a very small amount. This causes the iron to form magnetite, which covers the magnesite lining to almost any desired thickness and thus greatly prolongs the life. When this coating wears off in the course of the succeeding operations, it may be readily renewed during the next charge.

The main advantages of the basic converter over the acid converter are: the greatly decreased cost of lining; the use of much larger converters which make for labor and power economies; a lower-grade matte can be treated than in the acid converter; the copper in the slag is lower; low-grade ores can be used for flux that could not otherwise be treated profitably; there is less slop from the converters; and the copper is produced in a shorter time.

The slag from the converting process, containing as it does several per cent of copper, is too rich to be thrown away and is returned to the blast furnace or reverberatory, or may be treated in a slag-cleaning furnace. At some plants, it is the custom to pour the molten slag into the blast-furnace settler. This is done on account of the blast-furnace charge being so high in iron that the added iron from the converter slag is undesirable. The economy of this operation, however, is a disputed question as many metallurgists claim that the copper is not recovered to any great extent, but simply mixes with the great mass of blast-furnace slag and is lost.

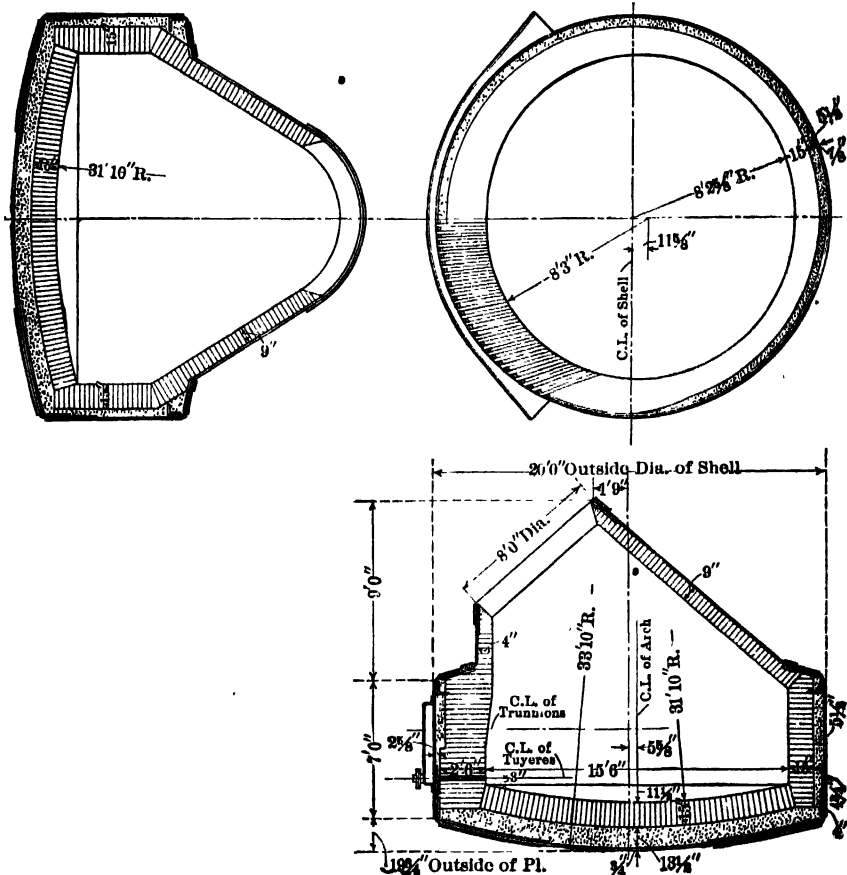


FIG. 3.--Great Falls 20-ft. basic converter.

**The Smelting of Oxide Ores.**—Where oxide ores occur, such as in the **Katanga** district, these are smelted in blast furnaces with a large percentage of coke. The product is known as black copper and its composition depends upon the impurities in the ore. A clean ore will give a high-grade copper, while, if much iron or nickel be present, these will be reduced and will lower the grade of the copper. Usually a small amount of matte is produced, due to the sulphur in the coke or small amounts of sulphides in the ore. Where there is little or no sulphur present, the copper losses in the slag are apt to be high, while a small matte fall tends to clean the slags.



The blister copper produced from any smelting process is generally cast into slabs approximating 18 by 28 in. and 3 to 4 in. in thickness, weighing 300 to 350 lb. There is just sufficient draft to the slab to permit of its ready removal from the mold. At some plants the practice still continues of casting the old type of Chile bar, which is about 8 by 20 in. with a thickness of from 6 to 8 in. This type of bar is very difficult to sample properly, on account of the segregation of the silver and gold, and it is also a difficult pig to handle easily. The Japanese frequently cast small slabs weighing in the neighborhood of 50 lb. each, which are very expensive to handle and sample, when considered on the ton basis.

Of late years, the question of moisture in blister copper has been given considerable attention. When a slab is cast, there are numerous cavities in the interior, due to the gases. These cavities are connected with the surface of the slab by capillary tubes, and if a slab is cooled by dumping it into a bosh, considerable water may be drawn into the cavities. It is not unusual to find slabs containing as much as 0.2 per cent moisture, and this question is the cause of much controversy between the smelter and the refiner as to what allowance should be made to cover this moisture (see p. 113).

In all smelting processes more or less flue dust is produced. The roasting furnaces are the chief offenders in this respect, though they are closely followed by the blast furnaces. The reverberatories having a relatively quiet atmosphere do not produce much dust, while that produced by the converters is largely in the form of fume from the volatile metalloids. The collection and retreatment of flue dust is a considerable item in the cost of operation, and every possible means is utilized to keep its formation down to the lowest point consistent with economical operation. The recovery of flue dust may be accomplished by one or more of the following methods: passing the gases through large dust chambers, in which the velocity of the gases is so reduced that all but the finest particles of dust are settled out. The gases may be filtered through woolen bags after being previously cooled to the proper temperature; this is an expensive method and requires a heavy investment in flues and bag house. The gases may be passed through a Cottrell electrostatic precipitator in which the solid particles are thrown out of the gas stream by the action of a high-tension electrostatic field. In the Roesing system, the gases flow through dust chambers in which are suspended wires or baffles, and the dust particles impinging upon these adhere, and when sufficient has accumulated the gases are diverted into another chamber and the wires or plates are then shaken to dislodge the dust particles.

The treatment of recovered flue dust consists in briquetting and smelting in the blast furnace, a method formerly widely used but now falling into disuse; agglomerating in rotary kilns, or Dwight-Lloyd sintering machines; and smelting in the blast furnace, or by direct smelting in the reverberatory furnace—the most economical method.

Metal loss is a very important item in the smelting cost, and one which is watched and studied very carefully so that it may be reduced to a minimum. The three chief sources are dust losses in handling, metal contents of slags, and dust and fume losses through the stacks. These losses are a matter of more importance to the custom smelter than to the company owning its own mines, as in the latter case the loss is merely that of the cost of the metal to the point of loss and the potential profit, whereas in the custom smelter the miner has been paid for the contents of his ore and losses represent the loss of actual profits.

**The Refining of Blister Copper.**—The blister copper produced in the smelting process contains so much impurity that it is unfit for commercial consumption without refining. The following table shows the composition of various grades of blister copper produced in the various smelters:

Cu %	Ag oz. p.t.	Au oz. p.t.	As %	Sb %	Pb %	Ni %	Zn %	Fe %	S %
98.8	4.50	0.01	0.004	0.002	0.018	0.41	0.016	0.15	0.10
99.5	2.50	0.02	0.035	0.015	0.001	0.04	0.002	0.03	0.06
98.8	30.25	0.31	0.10	0.040	0.150	0.050	0.120	0.25	0.17
98.4	111.9	0.295	0.02	0.178	0.001	0.005	0.003	0.13	0.20
99.10	73.3	2.09	0.01	0.01	0.048	0.005	0.036	0.056	0.25

In earlier days the refining of blister copper was performed entirely in reverberatory furnaces, but this has been entirely supplanted by the electrolytic process. Of the former process, it is sufficient to state that it was based upon the fact that when copper sulphide and copper oxide were melted together, the resulting reaction formed metallic copper, the sulphur passing off in the waste gases as sulphur dioxide. Silver and gold were recovered to a considerable extent by first having a small copper fall in the matte which served as a collector for these metals together with much of the impurities present. The enriched portion was worked up separately, while the purified white metal was carried along to pure metallic copper.

The modern process of refining may be considered to be divided into the following steps: (1) A preliminary fire refining, to remove as much as possible of the impurities, followed by the casting of the copper into anodes. (2) The electrolytic process, consisting in dissolving the anode by means of the electric current and depositing the pure copper on the cathode. In this step the remaining impurities are removed and any silver and gold contained in the anode are collected as a mud or slime to be recovered by a subsequent treatment. (3) A final furnace treatment of the cathodes, which are not in a form suitable for general commercial use, in order that they may be converted into the proper physical shape for the consumer.

**Furnace Refining.**—As the methods of operation of the anode and cathode furnaces are almost identical, one description will suffice for both. The furnace treatment is based upon the relatively weak affinity between copper and oxygen, as compared with the affinity between oxygen and the impurities in the copper. The process, therefore, consists in an oxidizing fusion in order to volatilize some of the impurities and to oxidize the remainder, using copper in the form of oxide as a scorifying agent. This being done, the impurities will either pass off in the furnace gases or else float on the surface of the bath as a slag which may be skimmed off.

As the remaining copper is now saturated with oxygen, the next step is to reduce the cuprous oxide to copper by means of some satisfactory reducing medium, after which the copper is cast into the necessary shapes.

In the anode furnace the blister copper should be refined to the highest degree that is economically possible in order to have a uniform high-grade product to send to the electrolytic process. This is necessary, as the success of the latter is largely governed by having uniform operating conditions, and it is generally much cheaper to eliminate impurities by a furnace treatment than by electrolytic methods. It is, however, not possible to remove the last traces of the impurities in the furnace. The great bulk is gotten rid of quite easily, but as the amount becomes reduced it becomes increasingly more difficult without slagging off so much of the copper that the treatment of the resulting by-products becomes too

expensive. Just where this point is depends upon local conditions and the relative cost of the two processes. There are also some of the impurities that tend to alloy with the copper and which are removed with great difficulty.

The reverberatory furnaces in which the refining is conducted are at the present time constructed with capacities of 500,000 to 600,000 lb. per charge. Due to the weight of metal contained, they are necessarily of much stronger construction than the reverberatory furnaces used in the smelting of ore. The side walls are constructed of silica brick with a thickness of 12 to 18 in., though there is an increasing tendency to use magnesite brick up to a point above the metal line, and then use silica or a good grade of clay brick from that point up to the roof.

The roof is almost invariably made of silica brick 15 to 18 in. in thickness, though attempts have been made to use fire brick or chrome brick. The great advantage of silica brick is its ability to withstand the temperatures obtained without softening and losing its shape. Fire brick softens at a low temperature, particularly when under pressure, while chrome brick absorbs a great deal of metal and it is difficult to treat the burned-out brick for the recovery of the copper contents.

The hearths of furnaces treating relatively pure materials are generally constructed of siliceous material, while magnesite brick is used where the copper contains considerable amounts of lead or antimony. The siliceous hearth is generally made of high-grade silica sand which has been crushed to the size of coarse sand. It may be used with an admixture of lime or copper oxide or may be put into place without any binder other than the natural impurities in the sand itself. The sand is mixed thoroughly and placed in the furnace, where it is given a thorough calcining, after which it is spread over the bottom to the desired depth and tamped down. The furnace is then gradually brought to the highest possible heat that the brickwork will stand until the new bottom is thoroughly sintered into place. Then the furnace is gradually cooled down and the bottom is then seasoned by covering it with a thin layer of scrap copper, melting this, and allowing it to soak into the bottom. The furnace is allowed to cool somewhat and the operation repeated until all the copper that will be quickly absorbed has been taken up. After this, small charges are introduced and the furnace is gradually brought up to capacity in the next few days. It is found that a furnace will absorb copper for a considerable period of time before becoming saturated. The amount of copper locked up in a bottom will depend upon the size and the shape of a furnace, but may be said to be in the neighborhood of 1,000 lb. per ton of daily capacity. The concentration of silver and gold in a furnace bottom will depend upon the grade of material treated, but will increase with continued use, the gold tending to concentrate to a greater extent than the silver. Very high silver charges will greatly increase the silver absorption, which will not be washed out by later charges of lower grade to any considerable extent.

Due to the danger of overheating the bottom and having a portion of it come up, the universal practice is to have a vault under the bottom to insure the proper amount of cooling. This may be supplemented by having pipes laid in the bottom through which air or water is forced to insure the necessary cooling. A bottom of magnesite brick will radiate more heat than a silica bottom, due to the greater heat conductivity, and in such construction it is necessary to have the magnesite brick underlain with a heavy backing of clay brick. This type of bottom is generally laid in the form of an inverted arch held in place by skewbacks attached to the side plates of the furnace. The brick should be laid dry or in a mixture of powdered magnesite and linseed oil. After laying it, the furnace must be very carefully dried out by the use of salamanders placed at different points along the hearth until all moisture has been driven off. If this is not done, there is great danger of the formation of superheated steam, which destroys the texture of the brick, and the entire bottom is liable to be rapidly destroyed.

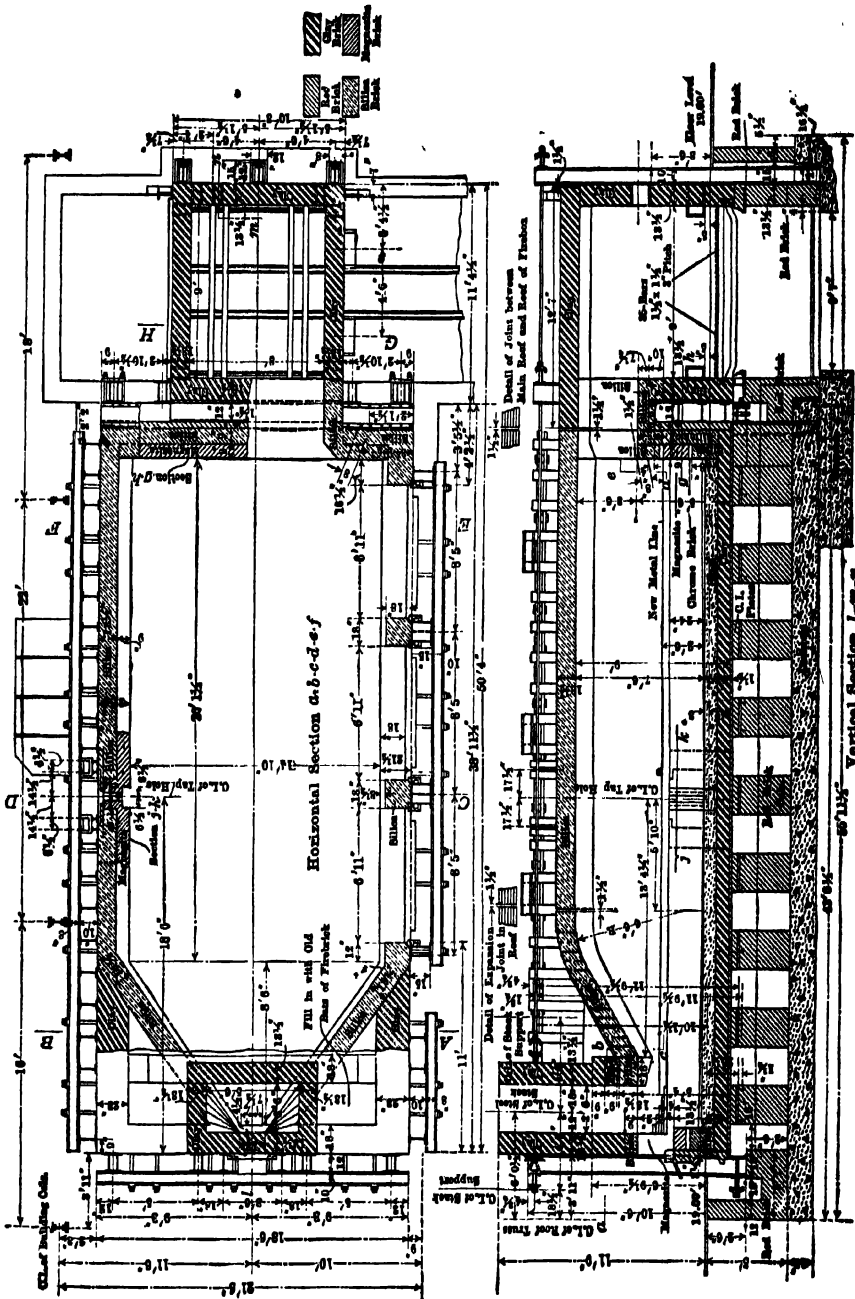


Fig. 4.—Copper refining furnace, United States Metals Refining Co., Carteret, N. J.

After drying out, the furnace is gradually brought up to a good red heat and the bottom seasoned as with a silica bottom.

The fuel used may be bituminous coal, pulverized coal, fuel oil, or producer gas. Producer gas is usually not available at most refineries and the modern tendency is to use either fuel oil or powdered coal. Hand firing is expensive and the question of ash disposal is bothersome. Powdered coal has the disadvantages of requiring the installation of a pulverizing plant and, as much of the ash of the coal remains in the furnace, the amount of slag produced is increased. Fuel oil has the disadvantage of requiring the installation of storage tanks, pumps, and preheaters for the oil. Either powdered coal or fuel oil is more economical than hand firing with an equivalent B.t.u. price, and the furnace temperature is much easier to control.

When hand firing with bituminous coal, the coal used will approximate 250 to 350 lb. per ton of copper; pulverized coal will reduce this 20 per cent, and with fuel oil the consumption will be about 22 to 26 gal. per ton using oil of 18,000 B.t.u. per lb. and 16 to 18°Bé.

It is now the universal practice to equip all reverberatories with waste-heat boilers to recover the large amount of heat in the waste gases. With coal, the recovery will be 6 to 8 lb. of steam per pound of coal and with oil 8 to 10 lb. of steam per pound of oil. In a large plant this waste-heat steam amounts to one-third to one-half of the steam used in the plant, so that the economy is obvious.

The dimensions of some refining furnaces are:

GENERAL DIMENSIONS OF SOME REFINING FURNACES<sup>1</sup>

	American Smelting & Refining Co.		Raritan Copper Works		U. S. Metals Refining Co.
Length of hearth.....	50 ft.	36 ft.	37 ft. 6 in.	43 ft.	40 ft. 3 in.
Width of hearth.....	14 ft. 7 in.	15 ft.	17 ft.	14 ft. 3 in.	14 ft. 4 in.
Depth of hearth....	22 in.	14-16 in.	35 in.	28 in.	30 in.
Hearth area, square feet.	665	490	559	553	496
Length of grate.....	9 ft.	Oil fired	Oil fired	.....	8 ft. 3 in.
Width of grate.....	8 ft. 4 in.	.....	.....	.....	7 ft. 4½ in.
Area of grate, square feet..	75	.....	.....	.....	60.8
Height of roof above hearth at bridge.....	6 ft. 4 in.	6 ft. 10 in.	7 ft. 9 in.	7 ft. 6 in.	7 ft. 2 in.
Height of roof above hearth at flue.....	3 ft. 6 in.	3 ft. 6 in.	5 ft. 10 in.	4 ft. 2¾ in.	4 ft. 9 in.
Area of flue, square feet. .	12 47	12.00	11.50	9 15	12 75
Tons output per 24 hours	200	178	250-275	275 325	226

<sup>1</sup> "Metallurgy of Copper," Hoffman-Hayward

The various operations of the furnace may be classified as charging, melting, oxidizing, poling, and casting, and will be taken up in their order. The large furnaces are charged by means of electrically operated charging machines which handle up to 6,000 lb. of copper at one time and which will charge a 200-ton furnace in less than 2 hr. In the smaller installations the old method of hand charging is still in use. This consists of placing the slabs of copper on a paddle and sliding them into the furnace. This is a slow and expensive method and is rapidly being displaced. Due to the large amount of space occupied by the slabs the amount that can be charged at

one time is usually less than the capacity of the furnace, and it becomes necessary to recharge a small amount after the original charge has been melted down.

When charging cathodes, a larger amount can be charged during the first charging, as they stack better and do not occupy as much space relatively. At the plant of the Nichols Copper Co. a unique method of charging is used, which consists of sliding the cathodes into the furnace by means of a chute. By this arrangement, the furnace is not permitted to cool down, and the fuel consumption is thereby decreased. With the charging crane the doors of the furnace must be opened, and by the time the furnace is charged it has cooled down to a dull red or black heat.

When the charging of the furnace has been completed, the doors are luted up and the fire urged to the utmost extent. As copper is an excellent conductor of heat, the metal rapidly absorbs the heat and soon starts to melt on the edges. During the melting, the flame is kept strongly oxidizing in order to have a sharp cutting heat and to form as much oxide as possible. When the surface of the bath is smooth, the firing is continued strongly until the metal on the bottom has melted, which is recognized by the charcoal or coke covering of the preceding charge rising to the surface. Between the time that the charge is flat and when the metal is afloat, the slags that form are skimmed. The amount of slag formed depends upon the nature of the material charged. Average blister copper will produce about 3 to 4 per cent of its weight of slag, cathodes about 1 to 2 per cent, and foul coppers may run as high as 30 per cent. With coal firing the ash of the coal is frequently blown over into the bath and forms slag, and with powdered coal there is a considerable increase, at times amounting to 50 per cent. Fuel oil, on the other hand, has no tendency to increase the amount of slag formed. As refinery slags are high in copper (30 to 50 per cent), it is seen that the retreatment charges are heavy and a small increase in the amount of slag formed is immediately reflected in higher costs.

When the metal in the bath has been skimmed clean, a say ladle, which is a small ladle with a long handle used for taking samples of the molten metal, is dipped into the furnace, and a test button taken to determine the condition of the metal. If, while the button is solidifying, it breaks through the crust and "throws a worm," this is indicative of sulphur, and a green pole is inserted in the bath to agitate the metal and drive out the sulphur held in solution by the copper. During this poling the atmosphere is kept strongly oxidizing. Buttons are taken frequently until the evidences of sulphur have disappeared. This operation is known as poling down. When the sulphur has been poled out the copper in the bath is oxidized by inserting air pipes through which compressed air is forced. This not only itself oxidizes the copper to a considerable extent, but, by the violent agitation it causes, exposes a large surface of the molten metal to the oxidizing influence of the hot gases. To assist the oxidizing a rabble may be introduced through the skimming door and by means of a chain suspension swung back and forth, breaking the surface of the metal into thin sheets or sprays. It is found that the rabble is more effective as a means of oxidizing than the air jets, but, owing to the great mass of copper to be oxidized and the hot and fatiguing work of swinging the rabble, its use as the sole means of oxidizing is impracticable.

During this period of blowing and flapping, buttons are taken to show the progress of the oxidation. As the amount of cuprous oxide in the bath increases, the surface of the button sinks and the fracture shows a color approaching a brick red. When the metal is saturated with oxide, there will be a deep depression, the fracture will show a bubble in the center, and the fracture will be coarsely cubical and a strong brick-red color. During this period, more or less slag will form and will be skimmed off, so that the surface of the metal will be kept clean for the action of the hot oxygen

in the gases. The cuprous oxide formed acts as a scorifying agent and is the effective means of removing the impurities in the metal.

When the buttons show that the charge is saturated with oxygen or "set," the air pipes and rabblers are removed and the surface of the bath is covered with coke or charcoal. The doors are closed and tightly luted up so as to prevent the admission of excess air. A pole is then inserted in the bath in order to reduce the cuprous oxide to metallic copper.

The poles used for this operation are usually hardwood, but softwood is readily usable, the chief objection being the heat developed at the poling door, with the attendant discomfort to the men, and more wood is required per ton of copper. An average amount of wood used for poling may be considered to be 100 to 150 lb. per ton of copper. If wood is used to make the charcoal covering for the bath, the amount is increased to 250 lb. per ton. As the pole burns away it is pushed further into the furnace, and when it becomes too short to hold by the chain block it is pushed into the furnace and becomes a brand, while a new pole is introduced.

During this time, test buttons are taken and the surface and fracture observed. The fracture gradually changes from coarsely cubical to finely granular, then fibrous, the color changing from a brick red to a salmon pink. When the poling is finished the surface of the button is slightly rounded, and the fracture is silky and of a rose color. The copper is now said to be "tough pitch" and is ready for casting.

During the progress of the refining the various impurities behave about as follows: Iron and cobalt oxidize and slag off readily, though if cobalt be present in any considerable quantity a considerable time may be required for its complete elimination.

Nickel is a very difficult element to slag on account of its strong affinity for copper. With high-nickel coppers the first few percentages of nickel readily pass into the slag, but as the amount decreases the slagging becomes slower and slower. To eliminate the last portions is extremely difficult. The bath must be skimmed clean, and, by continuing the oxidation, the nickel oxide forms as a powder and may be skimmed off. If, however, there is any reducing action in the furnace, the nickel easily reduces and is absorbed by the copper.

Sulphur requires a great deal of poling and oxidizing to effect its removal, and if present in blister copper to any considerable extent will make the furnace work very hot. If an excessive amount is present, there will result a great deal of trouble from the formation of matte on the surface of the bath.

Lead partly volatilizes and is partly slagged. With considerable lead present it may become necessary to throw the charge coarse with a small addition of matte and reoxidize. When present in any considerable quantity, lead will vigorously attack silica bottoms as soon as any oxide is present, and it may become necessary to use magnesite brick bottoms when handling blister high in this element. Zinc is readily oxidized and its elimination is simply a question of time of blowing.

Arsenic and antimony partly volatilize, but are eliminated with considerable difficulty. In some cases it becomes necessary to treat the bath with a flux of lime and soda in order appreciably to reduce the amounts of these undesirable elements. In severe cases it is necessary to give the copper a second refining.<sup>1</sup>

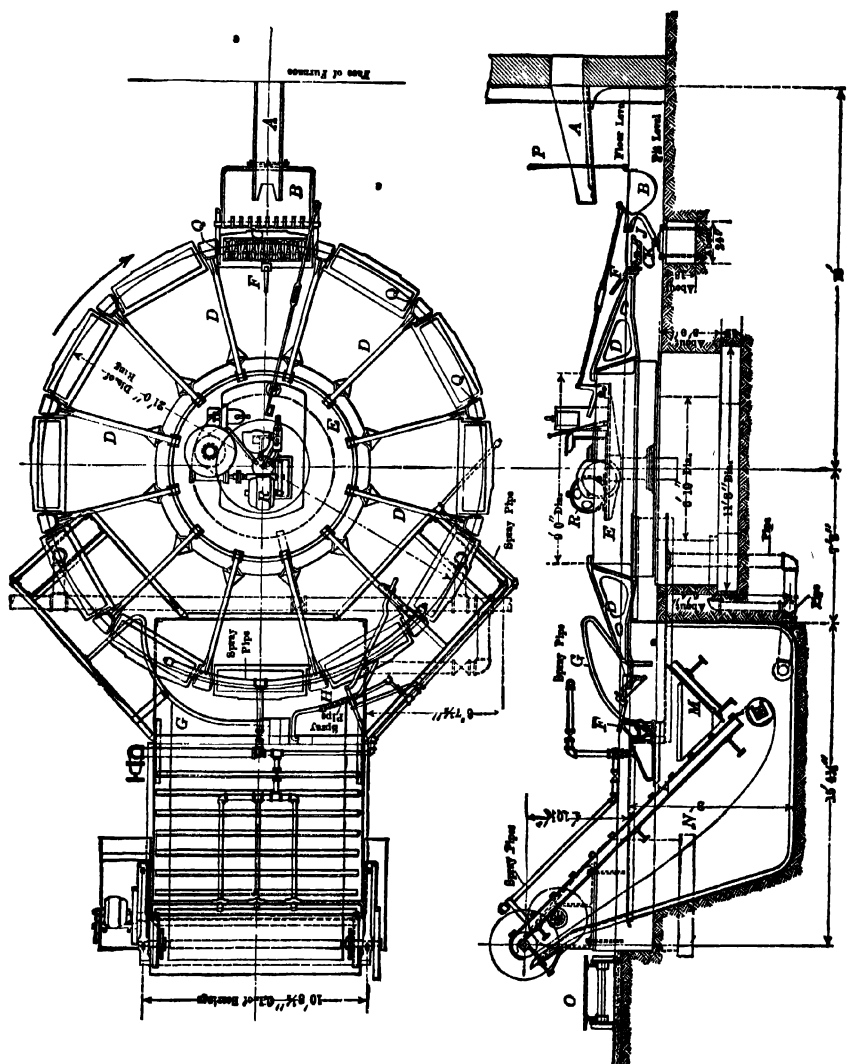
When the metal is finally ready for casting, that from the fire refining of blister copper is cast into anodes for the electrolytic process. For the multiple system these are slabs 24 by 36 in. or 36 by 36 in. and about 2 to 3 in. in thickness. When used for the series system, the anode may be cast as a slab for rolling, or as a long, thin anode for direct dissolving.

When the anode is to be used direct, lugs are cast so that it may be easily supported from the conductor bar or hanger bar. In some cases, loops of heavy copper wire are

<sup>1</sup> For researches on relative slaggability, see "The Mineral Industry," p. 248, 1901.

placed in the mold and the metal cast around them. A heavy copper bar is passed through the loops and is used to make the contact.

Where small furnaces are in use, the copper is frequently cast by hand ladling, but with the increased size of the furnaces it became necessary to find some faster method.



**FIG. 5.—Walker casting machine.**

It is now the universal practice with large furnaces to draw off the metal from the side or end of the furnace through a tapping slot. This slot or tap hole is filled with a mixture of clay sand and a small amount of coal, hard enough to withstand the pressure of the metal on the interior of the furnace, but soft enough to permit of cut-



ting a gutter for the flow of the metal. This plug is held in place during the working of the furnace by transverse iron bars, about 1 in. square, placed on top of one another and held by guides fastened to the side plates of the furnace. These bars are removed at the time of casting and the clay plug is cut away from the top sufficiently to permit the copper to flow over the edge into a launder leading to the ladle. As the level of the copper in the furnace falls, the clay plug is cut down more and more. If at any time it is desired to stop the flow of metal, a ball of clay is placed in the tap hole and pressed down with a stick.

There are several types of casting machines for the casting of anodes. The Walker wheel has the molds on the circumference of a wheel approximately 21 ft. in diameter. The wheel is turned by hydraulic or electric power and the molds are brought under the furnace ladle where they are stopped while the mold is filling. The wheel is then revolved until the next mold is under the ladle. When the newly cast anode is about three molds away from the ladle it is sprayed with water to cool the metal, and at the same time the mold is cooled by a spray from underneath. When the anode is nearly opposite the ladle it is lifted from the mold by means of a push pin which passes through the mold and slides on an inclined track. The anode is then lifted from the mold by a crane and placed in a bosh filled with running water in order to cool to the room temperature.

The straight-line casting machine consists of a series of molds carried by an endless belt in front of the ladle. When a mold is filled, it passes towards a bosh being sprayed on its journey, and at the end of the belt where the molds pass underneath the anode is either dumped into the bosh or else lifted out of the mold by a crane and placed in the bosh for cooling.

In hand ladling, the ladle man stands in the center of a wheel somewhat similar in shape to the Walker wheel, and, as each mold passes, it is filled with copper and passes around to the rear, where it is cooled and removed either by a hoist or by a man using a long-handled lifter.

Anode molds are generally made of copper, though in some instances cast-iron molds are used. The advantage of copper lies in the fact that when the mold has outlived its usefulness it can be charged into the furnace and the copper recovered and sold at market value, while a worn-out iron mold has only a low scrap value. In order to prevent the copper from sticking to the molds, they are washed with pulverized silica, which is applied at such a point that the heat of the mold will dry it out before the ladle is again reached.

The furnace refining of blister copper should be carried to the highest possible point in order to produce the best results in the electrolytic refining. A well-refined anode will dissolve readily and evenly and will give a good deposit, while an improperly refined anode will dissolve unevenly and give rough deposits and a heavy percentage of scrap which has to be retreated. It has been very clearly demonstrated that any extra expense incurred in the anode refining to insure a high-grade product will result in a much greater saving in the balance of the refining process.

The electrolytic refining of copper is based upon the selective action of the electric current in the following manner. If two metal plates are suspended in an electrolyte, and a direct current is passed from one plate to the other, the metal of the plate where the current enters, known as the anode, will be dissolved, provided the composition of the electrolyte is of the proper type. The plate at which the current leaves is known as the cathode, and what happens at this point depends upon the nature of the dissolved metal and the composition of the electrolyte. The constituents of the electrolyte are partly ionized and the individual ions have definite discharge potentials depending upon their positions in the e.m.f. series (see p. 678). Those ions having the lowest discharge potential will be discharged as long as they exist in sufficient amounts to carry the current. If there is an insufficient amount, the ion next

highest will be discharged. In an aqueous electrolyte the hydrogen ion is present and will be discharged unless there be present some other ion standing below it in the series. Copper is in this position and, therefore, will be discharged before hydrogen. The electrolytic refining of copper is, therefore, based upon the fact that, if a copper anode is suspended in an electrolyte composed of copper sulphate and sulphuric acid, it will be dissolved and the copper pass into solution. At the cathode, which is also copper, the copper in solution will be deposited while the hydrogen present will be unaffected.

The impurities associated with the copper in the anode do not deposit on the cathode because they stand higher in the e.m.f. series than either copper or hydrogen and, therefore, while they dissolve in the electrolyte, remain in solution, or else the composition of the electrolyte is so adjusted that they remain on the anode as insoluble alloys or compounds.

The impurities that, as a rule, pass into solution and remain there are Fe, Ni, Co, Zn, As, and Sb. Those that are insoluble and remain on the anode as a slime are Ag, Au, Pt, the rare metals, and Se, Te, and Pb.

Where an impurity exists in the anode as a chemical compound it will tend to pass into the slime, as chemical compounds have a much lower electrical conductivity than the copper, and these compounds largely segregate in the anode. The purer metal immediately surrounding them is dissolved, allowing the compound to fall into the slime, where it may lie inert or else be slowly attacked by the electrolyte and pass into solution. Those elements which alloy with copper may either dissolve or pass into the slime, depending upon their nature and properties.

Two systems of electrolytic copper refining are in use at the present time, the multiple and the series differing in the arrangement of the electrodes.

**The Multiple System.**—In the multiple system the anodes and the cathodes are connected in multiple and are suspended crosswise in a wooden lead-lined tank. The anodes are generally 2 by 3 ft. or 3 by 3 ft. in area, and from 2 to  $2\frac{1}{2}$  in. thick, weighing 400 to 600 lb. The number of anodes varies from 26 to 32 per tank, and they are given a spacing of about 4 in.

The multiple cathodes consist of pure copper starting sheets suspended between the anodes. The preparation of the starting sheets is an expensive operation, requiring skilled labor. In the manufacture of the starting sheets anodes of the purest grade of copper are used, and the anode is wider than the regular anodes to insure the edges of the starting sheet being perfect. The starting sheet is made by depositing copper on a rolled and stretched copper blank, which is coated with a mixture of graphite and oil, or else gasoline and oil, or other mixture that has been found to be satisfactory for the purpose. This coating is for the purpose of allowing the sheet to be readily stripped from the blank. To prevent copper being deposited on the edges of the blank, these are protected by covering them with grooved strips of wood, which are removed when the sheet is stripped from the blank, or else the edges of the blank are painted with a heavy asphalt paint, and a shallow groove is cut in the blank at the point where it is desired to have the sheet break off.

The process of manufacture of the starting sheet consists in first giving the blank a coating of the oil paint; the edges are then painted with asphalt or the wooden strips put in place, and the blank is hung in the tank while the current is on, and allowed to remain for the necessary time, usually 24 hr. The blanks are then drawn from the tank one at a time. The operator strips the thin sheet from the blank, with a sharp-edged knife, one sheet from each side, repaints it, and it is returned to the tank. The thickness of the sheet is usually about  $\frac{1}{16}$  in., and a 3 by 3 ft. sheet will weigh about 10 lb. It is of the greatest importance that the current be flowing when the

blank is placed in the tank or else the oil will be washed off by the hot electrolyte and the new deposit will be burned fast to the blank when the current is turned on. In order to hang the starting sheets in the regular depositing tanks two loops are fastened to each sheet. These loops are made of starting sheets which are cut into the proper-size strips and are fastened to the sheet by punching and bending back the sharp corners of the punched portion.

As the starting sheets must have good tensile strength, they are usually made at a current density lower than that used in the regular tanks, and the electrolyte used is kept very pure. The number of tanks required for this work will depend upon the number of cathodes to be drawn daily from the regular tanks, as a starting sheet must be produced for each cathode drawn.

The tanks used for the multiple system are built of long-leaf yellow pine lined with 6-lb., 6 per cent antimonial lead. The dimensions of a tank for thirty anodes with a surface of 3 by 3 ft. is approximately 11 ft. long by  $3\frac{1}{2}$  ft. wide by  $3\frac{1}{2}$  ft. deep.

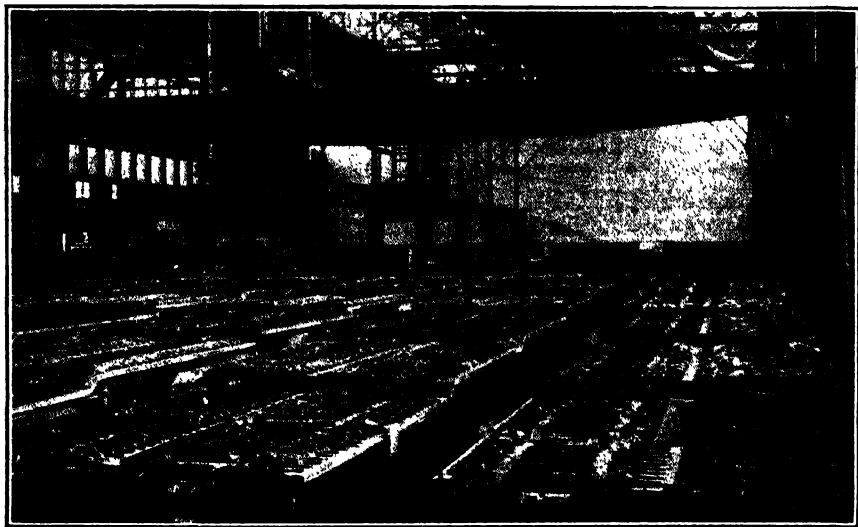


FIG. 6.—Interior Great Falls tank house.

Several arrangements of tanks are in use at the present time, the earlier arrangement being two tanks side by side and in rows depending upon the size of the tank room. As this arrangement required a large amount of copper to be tied up in bus bars, the Walker arrangement was developed, in which there are but two rows of tanks, but there are fifteen to twenty tanks, having a common partition, in each row. This arrangement effects a great saving in the amount of lumber needed, and, as the electrodes of one tank are connected to the electrodes of the adjoining tank by the use of a light triangular bar to which the cathodes of one tank and the anodes of the next tank are connected, there is a great saving in copper. This arrangement is at present the most widely used.

The tanks are built upon masonry piers high enough to permit of proper inspection underneath for leaks, etc. At the top of the piers are glass blocks having a thin sheet of lead placed on the top. The glass block serves as an insulator, the lead sheet protects the glass from any drip from a leaky tank. The tanks rest upon longitudinal sills 8 by 8 in., which rest upon the top of the piers. There are many variations in

the constructional details of the tanks, each refinery having its own ideas on the subject.

The electrical connections depend upon the tank arrangements. In the older system where two adjacent tanks are arranged in cascade of 8 to 10, the current is led to each pair of tanks by a heavy copper bus bar. The current leaving the cathode bar was conducted to the adjacent tank by means of a heavy copper connection plate upon which the anode bar rested. The current then left this tank through a heavy bus bar which led it to the next pair of tanks in the cascade. In the Walker system the current is led to the first tank by a heavy bus bar. The common partition between the tanks supported a light triangle bar upon which the cathode bars of the preceding tank and the anode bars or lugs of the succeeding tank rest. At the end of the row of tanks the current was carried by a heavy bus bar to the next row of tanks. There is thus a great saving in the amount of copper tied up in conductors when using the Walker system.

In the multiple system, as the electrodes are in multiple, each anode must have its individual current supply. With a depositing surface of 540 sq. ft. and a current density of 20 amp. per square foot the total current required will be 540 by 20, or 10,800 amp. per tank. With thirty anodes per tank each anode will require 360 amp. The use of such large currents requires conductors of large cross-section to prevent overheating and consequent loss of power, and this constitutes a large proportion of the initial investment in a multiple tank room. The generation of currents of this magnitude also requires expensive generating equipment in the power house.

The operation of the multiple system is about as follows: The anodes having been straightened are placed in the tank by an overhead crane and are then evenly spaced by the tank men. The starting sheets are straightened and a copper bar passed through the loop. They are then hung in the tanks and the loops securely clamped to the cathode bar by tongs specially designed for this purpose. This is done to insure a minimum contact resistance between the loop and the rod. The starting sheet is then accurately spaced between the anodes. All anode and cathode contacts with the bus bars or triangle bars are then given a coating of oil in order to prevent acid and salts from creeping in and spoiling the contact. The tank is then filled with electrolyte and the current turned on. At the end of 48 hr. it is customary to withdraw the cathodes one by one and straighten them, as the initial deposit has a tendency to make them curl slightly.

The time required for making a full-weight cathode depends upon the current density used, the quality of the anode, and various factors peculiar to the plant in question; but usually two cathodes are produced from each anode, and the time required per cathode is from 10 to 14 days. During this time the tanks are gone over daily and inspected for short circuits, and when these are found the cathode is lifted up and the nodule causing the short circuit broken off, or else it may be removed by the tank man sweeping a copper rod across the face of the cathode.

When the first crop of cathodes has run its full time, the tanks are cut out of circuit by short circuiting the entire section of tanks to be drawn by the use of a heavy copper cut-out. The cathodes are removed by an overhead crane and taken to a wash box, where they are thoroughly washed by a spray of hot water to remove any adhering slime and electrolyte. They are then piled on a car and sent to the wire-bar furnace.

The anode mud which contains the silver and gold is then swept from the face of the anode by means of brushes with long handles, or else the anode may be withdrawn from the tank and taken to a wash box, where the slime is washed off by hot water and the anode returned to the tank. A new set of starting sheets is placed in the tank, the contacts gone over as before, and the current turned on. During this second run of cathodes the anodes are carefully watched to see when they become too thin for

proper working. When an anode gets scrappy, due to its being thinner than it should be, or else having dissolved at a faster rate than its mates, it is withdrawn from the tank and replaced by a piece of heavy scrap, a supply of which is kept on hand in the tank room—for such purposes.

At the end of the run the tank is cut out of circuit as before, the cathodes removed, washed, and shipped, and the scrap anodes drawn from the tank by the crane and thoroughly washed to remove all adhering slime. They are then sent back to the anode furnace for remelting. Any heavy scrap is generally kept in the tank room for the purpose, described above, of replacing anodes that have gone scrappy before their time.

The electrolyte is pumped out of the tanks and a plug in the bottom of each tank is removed, and the accumulated slime is flushed into a launder, which conveys it to a slime tank, where it is screened to remove coarse pieces of metallic copper and is then pumped to the silver refinery for the recovery of the precious metals contained.

The tank is thoroughly cleaned of all adhering salts and slimes, any leaks that may have developed are repaired by the lead burners, the triangle rods are cleaned of salts and dirt, and the tank is then ready for another run.

The amount of scrap made in the multiple system will depend upon the character of the anode, the current density, and the care taken in casting the anodes uniformly thick. The usual practice will make about 15 to 20 per cent scrap, a large part of which is accounted for by the lugs which are not dissolved. The percentage of scrap made is kept as low as possible on account of the retreatment cost, the tie-up in metals, and the delay to putting in process contract material.

**The Series System.**—In the series system the electrodes are connected in series and the same current serves each electrode. There are no starting sheets as the back of each anode serves as the cathode for the preceding anode.

There are two modifications of the series system: In one a rolled anode is used, in the other a cast anode is used. The first is in operation at the plant of the Baltimore Copper Co., the second at the plant of the Nichols Copper Co.

At the Baltimore plant the anode material must be of good quality to permit of rolling without cracking. The anode furnaces cast a slab, which, while red hot, passes through the rolls and is rolled down to a thickness of about  $\frac{1}{4}$  in. It is then cut into plates approximately 11 by 24 in., which are straightened and two plates placed in wooden frames, which are placed in the tank. The tanks are 11 ft. 6 in. in length, 25 in. in width, and have a depth of 26 in.; 135 electrodes are placed in each tank.

The current enters the tank through the first electrodes, passes through all the electrodes in series, and leaves through the last electrode, which is a copper plate. The electrodes act as both anodes and cathodes, the side receiving the current being the cathode, and the side from which the current leaves being the anode. As a result, the impure metal of the anode is dissolved from one side of the plate while pure copper is deposited on the other side of the plate to approximately the same thickness.

The deposition is finished when the anode has been dissolved to the desired degree, which is usually a complete dissolving, so that there is little or no scrap, other than that from the rolling and the cutting of the plates and that left in the grooves of the strips. The cathodes are removed from the tank, washed, and sent to the wire-bar furnace. The slime remaining at the bottom of the tank is removed by hand and the tank is carefully cleaned out before the next run.

At the Nichols plant the anodes are cast, and average 12 by 54 by  $\frac{5}{8}$  in. They are straightened, and the cathode side is painted with a mixture that will permit of readily stripping the cathode from the undissolved portion of the anode. The anodes are then hung on an iron bar, there being five anodes to a bar, and 121 bars are hung in a

tank. The tank is then filled with electrolyte and the current turned on. When the deposition has proceeded to a point where the amount of anode remaining is about 8 per cent, the deposition is considered finished, the electrodes are removed from the tank by a crane, and carried to the stripping room where the remaining anode scrap is removed and sent back to the anode furnace for retreatment, the cathodes being sent to the wire-bar furnace, and the slime flushed out and sent to the silver refinery.

The current density used in the series system is the same as that used in the multiple system, but as the electrodes are in series the amount of current per tank is much less. Where a multiple tank having a depositing surface of 540 sq. ft. requires a current of 10,800 amp., a series tank having a depositing surface per plate of 4 sq. ft., as at Baltimore, or 23 sq. ft., as at Nichols, will require 80 or 460 amp., respectively. These small currents avoid the use of conductor bars of large cross-section, and, as there are but few contacts per tank in the series system as against approximately 120 in the multiple system, the contact losses are reduced to a minimum.

The voltage across the electrodes in the series system at the solution level is approximately the same as that in the multiple, for equal spacing, so that, while the multiple system has a low voltage per tank, the series system, which in reality consists, electrochemically, of a number of multiple tanks in series, has a voltage corresponding to the number of electrodes in series. Where the multiple system has a voltage at the solution level of, say, 0.2 volt, the series tank, with 135 electrodes, will have a voltage of 27.0 volts, and with 121 electrodes the voltage will be 24 volts, if the electrode spacing is the same in all cases. The electrode spacing in the series system, however, is closer than in the multiple system, and the voltage is correspondingly reduced.

The overall voltage per electrode in the series system is much less than in the multiple, therefore, both on account of the closer spacing and the almost complete absence of contact resistances. The average voltage may be taken as about 20 volts per tank at a current density of 20 amp. per square foot.

This high voltage makes it necessary to use tanks having an insulating lining, and the lead-lined tanks used in the multiple system are not practicable. The usual construction is either of wood lined with some asphalt compound, slate, or else concrete lined with asphalt, the last being preferable, due to a longer life and cheaper maintenance.

The multiple and series systems may be roughly compared as follows: The multiple system casts heavy, thick anodes; the series requires rolled or light, thin cast anodes. The multiple system requires the preparation of a special starting sheet, which is an expensive operation requiring skilled labor. The series system uses no starting sheet, but it is necessary to strip off the backs, an operation performed by common labor. The multiple system requires heavy currents per tank, necessitating heavy conductor bars with a consequent large tie-up of copper. The series system uses low currents and avoids the use of heavy conductors.

The copper produced per kilowatt-day in the multiple system at a density of 18 amp. will average about 165 to 180 lb. In the series system the production per kilowatt-day will average about 340 to 380 lb. The power requirements in the series system are thus about half those in the multiple system. The efficiency in the multiple system will average about 90 per cent, in the series system about 70 per cent, due to the current leaking past the plates. The scrap produced in the series system is less than that produced in the multiple system with a consequent less cost for retreatment. The greater output per tank in the series system requires less tanks for any given output. The tanks used in the series system must be lined with insulating material. In the multiple system lead linings are used. The metal losses in both systems are about equal, while the copper, silver, and gold locked up in process are less in the series than in the multiple.

Outside of the shape and arrangements of the electrodes and the tanks, the other features of electrolytic refining are common to both processes. The electrolyte has a composition of approximately 35 g. per liter copper, 140 to 200 g. per liter sulphuric acid, together with small amounts of such impurities as iron, nickel, arsenic, and antimony as may accumulate from the dissolution of the anode. The electrolyte has a marked negative temperature coefficient and, therefore, is heated by steam to increase its temperature and reduce the electrical resistance. The degree of heating used depends upon the relative cost of power and steam as well as the electrolyte composition, to a certain extent. The usual temperature is about 130°F. As the power used in overcoming the resistance of the electrolyte appears therein as heat, there is considerable heating from this source. The amount of steam used in the multiple system per tank will be greater for the same temperature than in the series system, due to the different amounts of power developed in the tanks. A multiple tank will develop approximately 3 kw. while a series tank will develop about 10 kw.

Due to the tendency of the electrolyte to segregate under the action of the current, it becomes necessary to circulate it through the tanks. The segregation is more marked in the case of high-current densities than in low densities. It is caused by the fact that at the face of the anode, where copper is passing into solution, the electrolyte consists largely of copper sulphate of high specific gravity and there is a tendency to stream downwards. At the face of the cathode, where copper is removed from the electrolyte, the latter becomes largely sulphuric acid of lighter specific gravity and the tendency is to stream upwards. If, therefore, there were no circulation at all, the electrolyte would soon form two distinct layers, that on top being high in acid and low in copper, while the bottom layer would be high in copper and low in acid. As a result, the deposition would be largely confined to the lower part of the cathode, while there would be a copious evolution of hydrogen at the top of the cathode accompanied by spongy copper. The efficiency would, therefore, be greatly decreased, and the power per ton of copper increased. With an adequate circulation this tendency is counteracted to a large extent and the deposit kept regular. The higher the current density the greater will be the amount of circulation required to prevent stratification. On the other hand, an increased circulation tends to keep the slime in the tank stirred up, resulting in increased metal losses. The choice, therefore, lies between greater efficiency of deposition as against increased metal losses. The normal rate of circulation will be about 3 to 4 gal. per minute for current densities of 15 to 20 amp.

At some plants the electrolyte is admitted at the top of the tank and withdrawn from the bottom, while at others the flow enters at the bottom and is withdrawn at the top. The latter requires less solution and there is less danger of a tank being flooded. This is because the solution on cooling becomes denser and, therefore, a greater head of the hot, entering solution is required to force the cooler solution from the bottom of the tank; and in case the current has been off for some time, so that the solution has become quite cool, the head required to raise the cold column of solution in the outlet pipe may be such that it is more than the tank will hold. On the other hand, the objection to the top overflow is that this type of circulation opposes the natural settling of the slime. As, however, the rate of flow per square foot of cathode surface is exceedingly small, this objection appears to be more theoretical than actual.

The older plants had their tanks arranged so that the electrolyte flowed through as many as six tanks in cascade. This practice reduced the amount of electrolyte required, but the great cooling that occurred so increased the resistance that the loss in power more than offset the reduction in the tie-up of metal in solution. The modern practice is, therefore, to reduce the number of tanks in cascade to one or two,

thus preventing severe temperature inequalities and giving better efficiency and power consumption.

**Circuit Resistance.**—The current used in the electrolytic refining is, of course, direct current, and the amount carried by the bus bars will vary from 10,000 to 12,000 amp. for the multiple system to 500 in the series system. As the output depends upon the current, while the power depends upon the resistance, and the problem in electrolytic refining is to obtain the greatest output per unit of power, the question of resistances must be given very careful attention. The following resistances are encountered in the various systems:

**Multiple.**—Bus bars, bus-bar joints, anode contacts, anode, electrolyte, cathode, cathode loops, cathode-loop contacts, cathode rods, cathode-rod contacts, and other small resistances, such as resistance of the slime layer on the anode, transfer resistance, counter e.m.f., etc. The magnitude of these resistances is approximately as follows: contacts, 15 per cent; electrolyte, 60 per cent; conductors, 15 per cent; counter e.m.f., 5 per cent; slimes, etc., 5 per cent. In the series system there are the following resistances: bus bars, anode rod, anode hangers, anode, electrolyte, cathode, cathode hangers, cathode rod, and also the other small resistances mentioned in connection with the multiple system. The magnitude of the above is approximately as follows: contacts,  $2\frac{1}{2}$  per cent; electrolyte, 85 per cent; conductors,  $2\frac{1}{2}$  per cent; counter e.m.f., 5 per cent; slimes, 5 per cent. As the cost of power is one of the chief items in the refining of copper, constant effort is given to means whereby these resistances may be reduced and power saved.

Some of the ways in which savings may be made are as follows:

**Conductors.**—As the resistance of any conductor varies as its cross-section it is evident that any increase will result in decreased resistance. An increase in cross-section, however, will increase the weight and, therefore, the cost of the conductor. Thompson's rule that the most economical cross-section is that for which the interest on the investment equals the cost of power lost is applicable in this case, particularly for bus bars. For the other conductors in the tank, conditions prevent its application. Thus the anode lugs must be of sufficient strength to support the weight of the anode, and hence are usually of far greater cross-section than required for the current. As the cathode loops are made of thin, copper strips, these are generally of insufficient cross-section and hence carry a current density greatly in excess of that which is most economical.

**Contacts.**—The reduction of this resistance calls for two things: first, ample area of the contact surfaces; second, the elimination of as many contacts as possible. This resistance is one of the largest in the tank room, outside of that of the electrolyte, and much ingenuity has been shown in reducing it. Formerly, anodes were suspended by two hooks, giving five contacts, two at each hook, and one at the contact of the anode bar with the bus bar. The modern anode has but one contact due to cast lugs being used which make the contact with the bus bar. Cathodes were formerly suspended by hooks which have been replaced with firmly attached loops, the attachment being below the surface of the solution, where they soon become covered with the deposit and become an integral part of the cathode. An attempt has been made to eliminate the contact between the cathode rod and the triangle rod by having the cathode rod rest directly upon the anode lug in the adjacent tank.

One of the best methods of keeping contact losses at a minimum is to keep them clean. As there is generally considerable heat generated at any contact, any solution that may be splashed thereon will soon be converted into anhydrous sulphates, which prevent an effective contact. The most effective way so far developed for the



prevention of this formation is to apply a thin coating of oil to the contact surfaces. This will keep them clean for a long time and costs little to apply.

While the numerical value of each contact loss appears to be so small as to be almost insignificant, it must be remembered that there are a great many of these contacts throughout the tank room and their cumulative effect is sufficiently large to amount to a considerable waste of power.

**Electrolyte.**—The resistance of the electrolyte is affected by its temperature and composition. The temperature coefficient is negative, so that an increase in temperature decreases the resistance. The higher it is possible to carry the temperature the lower will be the resistance. There is, however, a practical limitation to the degree of heating on account of the cost of the steam exceeding the saving in power beyond a certain point, depending upon local conditions. Too high a temperature may also affect the character of the deposit, and the higher the temperature the greater the amount of evaporation and the higher the humidity in the tank room with its attendant discomforts.

The composition of the electrolyte has a great effect upon its resistance. As the conductivity is dependent upon the presence of hydrogen ions, an increase in the content of acid will increase the number of hydrogen ions present and decrease the electrolyte resistance. The presence of sulphates increases the resistance. These sulphates are not only the copper sulphate composing the original solution but also the accumulated sulphates from the impurities in the anode, such as iron, nickel, zinc, etc. To secure an electrolyte of minimum resistance it is necessary to keep the free acid as high as possible and the sulphates as low as possible. The practicable limits to high acid and low sulphates are that there must be a sufficient amount of copper in the vicinity of the cathode so that only copper ions will be discharged. This limitation, therefore, requires the copper to be kept not lower than 30 g. per liter in average work. If the acid is too high the saturation point of the sulphates present becomes very close to the operating temperature of the solution, and any cooling that may occur is likely to cause a salting out of these sulphates on the cathode, giving a very rough and contaminated deposit. The lower the contained sulphates in the solution the higher can the acid be maintained.

**Counter E.m.f.**—The cause of the counter e.m.f. is largely due to the formation of concentration cells at the electrodes due to differences in the composition of the electrolyte. This may be overcome to a certain extent by increasing the rate of circulation of the electrolyte, but there is a very practical limit to this on account of the danger of stirring up the anode slime and contaminating the cathode, thereby increasing the metal losses and producing impure copper.

The formation of concentration cells at the surface of the cathode also causes the copper content of the electrolyte to increase, due to the fact that, if at the top of the cathode there is a solution containing higher acid and lower copper than contained by the solution at the bottom of the cathode, a concentration cell will be set up and copper will tend to pass into solution at the top of the cathode and be deposited at the bottom of the cathode. But as the efficiency of deposition is less than that of dissolution the copper in the solution will increase, and this amount of increase will be greater the greater the difference in solution composition.

**Slimes.**—The resistance of the slime adhering to the surface of the anode will depend largely upon the purity of the anode. A high-grade anode produces slime that has low electrical resistance, while an impure anode gives a slime that

may have a very high resistance, and should the nature of the slime be such that it covers the anode with a very heavy, dense layer, the anode may be made almost insoluble with a correspondingly great increase in the voltage necessary for the operation of the tank.

**Current Density.**—The current density to be used in electrolytic refining depends upon a number of factors. It is of great importance, as the design of the tank room depends upon it. The two main factors affecting the selection of current density are the cost of power and the average composition of the anode. As the power cost varies directly as the square of the current density, a point is soon reached where the power cost becomes prohibitive. When the anode contains a large amount of silver and gold, a high current density will tend to give high metal losses in the cathode, due to the necessity of maintaining a high rate of solution circulation.

A high current density generally increases the labor cost because the weight of the cathode is more or less fixed by the physical labor of handling and a high current density means pulling cathodes of younger age. This more frequent pulling also requires the use of a larger number of starting sheets, the preparation of which is an expensive item. The question of interest on metals locked up in process plays a very important part in the determination of current density. If the anodes are high in silver and gold, the saving due to getting these metals on the market earlier will often pay for an otherwise uneconomical current density.

Increased current density requires the use of fewer tanks and less building space for a given output. This means a lower initial investment, and where construction costs are high, may have great influence on the question.

The average current density in use at the present time will vary from 15 to 20 amp. per square foot of cathode surface. In many cases this density is too high for present power costs, but as the plants were designed at a time when power was cheaper than at the present, it was correct at that time, and the only way in which the density can be reduced without building additional tanks is to curtail the output, and the loss sustained in so doing may be much greater than the loss due to increased power costs.

**Current Efficiency.**—The term current efficiency is an expression of the ratio of the amount of product actually obtained to that theoretically obtainable in accordance with Faraday's law. It is always less than unity on account of various factors, such as current leakage, short circuits in the tanks, and the deposition of hydrogen at the cathode. As the output of the tanks is directly proportional to the current efficiency obtained, other things being equal, a great deal of careful study is given to the maintenance of as high a current efficiency as is economically possible.

Current leakage in a well-designed plant should be small. It will vary with the voltage on each circuit and the care taken to keep the tank surfaces in a good, clean condition. The higher the voltage on any circuit the greater will probably be the leakage. The amount of leakage may approximately be determined by opening the circuit in the middle and taking the ammeter reading when the voltage is normal. As this method applies the full voltage to but half the tanks, however, the indicated leakage is apt to be somewhat higher than the actual amount. Another method is to compare ammeter readings at several points in the circuit, care being taken to guard against the stray fields that exist in the neighborhood of conductors carrying heavy currents. Leakage through the woodwork of the tanks should be negligible, provided<sup>1</sup>

they are kept in proper condition, and it may be assumed that the largest part of the leakage is through the circulating system, by the current being shunted around the middle tanks in the circuit, as the circulating system is in parallel with the depositing system. To prevent this leakage as much as possible the resistance should be made as high as possible by having the overflow pipes of considerable length and small cross-section. Where the leak occurs to the ground there is usually evidence on account of the copper deposited at the point where the current leaves the electrolyte.

The greatest part of the loss in current efficiency is due to short circuits in the tanks. These are caused by the following conditions; the new starting sheet may curl after a few hours in the tank and unless this is discovered and rectified a bad short circuit may result. To prevent this occurrence the starting sheets are generally removed from the tank, straightened, and replaced after a certain number of hours working. If the electrodes in the tanks are not properly aligned, there will result more or less short circuits due to the unequal current distribution in the tank. The tank men when working on top of a tank may kick an electrode out of place and neglect properly to replace it. As the anode dissolves away, pieces of the scrap may fall off and rest against the cathode.

Except at a low current density it is not possible to produce a perfectly smooth deposit with a cathode of any considerable age, and under normal working conditions the cathodes soon become more or less rough. When this occurs the resistance between the anode and the projecting part of the cathode becomes less, and there is consequently a greater tendency for the current to flow across this part, increasing the current density at such a point and aggravating the condition. If not corrected in time, the roughness will develop into trees which bridge across the space between the anode and cathode, resulting in a dead short circuit which may stop all depositing in that particular tank. To prevent such a condition the tank men continually patrol the tanks with voltmeters and long copper rods. When the voltmeter indicates the presence of a short circuit the rod is swept across the space between the anode and the cathode and the projection broken off.

Deposition of hydrogen at the cathode is due to an insufficient amount of copper ions to carry the current. This condition may be caused by too low a circulation rate or by the circulation being unevenly distributed between the electrodes. It may also be caused by the copper content of the electrolyte being too low or the acid content being too high. The usual cause is probably an inefficient distribution of the circulation throughout the tank. The current efficiency may be reduced as much as 5 to 10 per cent, due to this cause.

**Electrolyte Purification.**—As the impurities in the anode accumulate in the electrolyte, the resistance of the latter increases, resulting in a greater power consumption, and there is also danger of the cathode being contaminated. This contamination is in addition to the contamination from adhering slime and is due to the fact that the deposited metal on the cathode is always more or less porous. This porosity permits a certain amount of the electrolyte to become entrained, and contamination from this source will not be removed by the usual washing received by the cathode prior to its charging into the wire-bar furnace. The higher the current density the greater the tendency for porous cathodes. The addition of a small amount of glue to the electrolyte results in giving a denser deposit, but usually increases the resistance of the solution. The remedy for such contamination is to keep the electrolyte as pure as possible by constant withdrawals and replacement with fresh solution. The purification of tank-room solutions is a source of considerable expense unless the impurities have a marketable value.

The various methods of purifying the electrolyte are by the manufacture of bluestone, and by the use of insoluble anode tanks with or without the recovery of the sulphuric acid.

In the manufacture of bluestone, the hot electrolyte is passed through towers containing shot copper until the free acid is brought down to about 1 per cent. The solution is then concentrated with steam coils in lead-lined tanks and sent to the crystallizing tanks where the copper sulphate is allowed to crystallize on lead strips. These crystals may be sold or else redissolved and sent back to the tank room. The mother liquor from this crystallization contains the impurities, and if the impurity is of value, such as nickel sulphate, it may be further evaporated and the nickel sulphate crystallized out, after any traces of copper have first been removed. Otherwise the foul solution is wasted after precipitating out the remaining copper on scrap iron.

When using insoluble anodes the solution to be purified is passed through a series of tanks containing anodes of hard lead. These tanks may be used either for the reduction of the amount of copper in the electrolyte or for the complete removal of the copper prior to the final treatment of the solution. Where it is simply desired to reduce the amount of copper in the electrolyte the latter is circulated through the tanks at a high rate and returned to the tank room. The high rate of circulation is desired in order that the efficiency of deposition may be as high as possible and also that the quality of the cathode produced be high enough to be sent to the wire-bar furnace. Where it is desired to remove the copper completely, the circulation is reduced. There are usually three to five tanks in series and the copper from the first tank is generally of good enough quality to send to the wire-bar furnace. The product of the remaining tanks will, to a large extent, depend upon the composition of the electrolyte being purified. As the copper becomes depleted, arsenic and antimony are deposited as a sludge, which is generally sent to the blast furnace, if there be one at the plant, or else treated by special methods. The last tank eliminates the last traces of copper from the electrolyte. The efficiency of these tanks is very low, the average for the series being about 20 per cent or less.

If arsenic and antimony are the impurities to be eliminated, the solution is returned to the tank room. If there is a large amount of soluble sulphates, such as iron, nickel, or zinc, the solution from the insoluble anode tanks is either sent to the sewer and the acid content wasted, or else it may be concentrated by heating to such a point that, upon cooling, the objectionable sulphates are crystallized out. The mother liquor, which is high in free acid, is then returned to the tank room.

The use of the insoluble anode requires considerable power, but the investment required is small, whereas a large investment is required for the manufacture of bluestone. If, however, large amounts of solution are required to be purified, there is danger of depleting the electrolyte of copper to too great an extent. This is particularly true when the anode contains considerable amounts of nickel or iron, so that there is much less copper being dissolved than deposited. In such a case it becomes necessary to add copper to the electrolyte by means of bluestone or by trickling hot electrolyte through towers containing shot copper. On the other hand, with a pure anode there is a building up of the copper contents of the electrolyte, and this excess will have to be removed by one of the above methods.

The insoluble tanks are usually in two groups, the first of which has a high rate of circulation and removes the bulk of the copper, the second group removing the balance of the copper together with such arsenic and antimony as may be present. As the power consumption of insoluble anode tanks is high, an attempt has been made to eliminate the first set by utilizing the principle of the stratification of the electrolyte.<sup>1</sup> In this method advantage is taken of the fact that at the face of the anode

<sup>1</sup> PYNE, *Trans. Am. Electrochem. Soc.*, **28**, 111.

there is a downward flow of the electrolyte due to the increase of copper concentration, while at the face of the cathode there is an upward flow due to the decreased copper concentration. By withdrawing the main bulk of the electrolyte from the lower part of the tank and about 10 per cent from the upper part, there is obtained from the lower outlet a solution high in copper and relatively low in acid, while from the upper outlet the solution is low in copper and relatively high in acid, the copper being less than is usually obtained from the outlet of the first group of insoluble anode tanks. As the impurities do not segregate, the solution from the upper outlet contains practically the same amount of impurities as the average solution in the tanks. This method thus saves the extra cost of one group of insoluble tanks, and produces a cathode similar to those obtained from the regular refining tanks, with the expenditure of little, if any more, power than required for the production of regular cathodes.

The cathodes from the electrolytic refining, having been washed, are sent to the wire-bar furnace. This type of furnace is similar to that described under anode casting, but the operation requires more care, particularly in the poling operation and casting. Great care must be taken to have the metal at the proper heat, as cold copper will result in bars which are porous. Hot copper will absorb gases from the gases of combustion and these gases will be liberated on cooling, giving porous copper.

Overpoling causes the surface of the bar to rise and throw out a worm, and the resulting metal will very likely be brittle. The causes of overpoling are not definitely known, but it is believed that sulphur plays an important part.

Refined copper is cast on the Walker wheel or the straight-line machine, as described previously. The Clark wheel is a modification of the Walker wheel with the molds placed radially instead of tangentially, and bars of any length can readily be cast thereon.

The commercial forms of cast copper are wire bars, cakes, slabs, ingots, and ingot bars. Wire bars are bars of approximately square cross-section, the length varying from 40 to 60 in., the width and depth from  $2\frac{1}{2}$  to 4 in. The ends are usually tapered to facilitate admission to the rolls in the rolling mill. The weight of wire bars varies from 135 to 300 lb. according to the demands of the consumer. Cakes are square, or rectangular castings, varying in dimensions from 14 by 17 in. to 42 by 42 in. The thickness depends upon the weight desired for any particular cross-section and varies from 2 to 8 in. Cakes under 28 by 28 in. are generally cast on the casting machine, the larger ones being cast in open, iron split molds, placed on a copper base. Slabs are long, thin, shallow bars, usually with square ends. Ingots are small castings weighing about 20 to 25 lb. and have one or two heels cast to permit being broken up easily by the consumer. Ingot bars are bars consisting of several ingots end to end.

When casting refined shapes the molds are painted with bone ash. This gives a smoother surface than the pulverized silica used in the anode casting. For satisfactory work, the bone ash must be thoroughly calcined, be free from grease and organic matter, and must be very finely ground, 95 per cent to pass 200 mesh. It must be applied uniformly to the molds or the excess will cause the bars to be pitted.

When casting refined copper, great care must be used. If the mold is filled too rapidly, there will be a tendency for some of the copper to run up the side of the mold and set there. Excessive vibration of the casting machine has the same effect. Unless these fins are removed by chiseling before rolling, they will be rolled into the finished rod and cause trouble. Particles of ladle lining, charcoal, etc. are known as fish and are removed during the casting and before the metal has set by the use of a long-handled, flat-bladed tool.

Over- and undersized bars are caused by the molds being out of level, warped, or by the carelessness of the operator in filling the molds. An oversize bar may cause trouble in the rolling mill by crowding the roll and thus producing a fin which is rolled into the product. Undersized bars cause no damage in the mill, but add to the

expense of rolling due to the shortage in weight which requires more pieces to be rolled for the same tonnage.

As the bars set, they are sprayed with water and dumped into a water-filled bosh to cool sufficiently to permit of handling and inspecting. The inspection is very rigid, and bad looking bars are rejected and remelted. The bars that pass the inspection are stamped with the furnace and charge number for future reference in case of complaint.

The quality of the copper is determined by assay and by taking a sample for conductivity. While the assay will show the purity of the metal, which generally is about 99.93 to 99.96 per cent, the conductivity test is relied upon to show the physical qualities. Small amounts of impurities have, in general, a very marked effect upon the conductivity of copper, and while those elements which make copper brittle do not, for the most part, affect the conductivity to any great extent, their presence will be detected in drawing the wire for conductivity purposes.

**Treatment of the Anode Slime.**—The anode slime contains all of the silver and gold that is present in the anode, disregarding the insignificant amount lost in the cathode. It will also contain varying amounts of arsenic, antimony, selenium, tellurium, nickel, and a certain amount of copper, depending upon the degree of refining the anode.

At the tank room the slime is generally passed over a coarse screen to remove large pieces of copper, such as anode scrap, cathode nodules, etc., and is pumped over to the silver refinery, where it is allowed to settle in tanks of large cross-section. The supernatant liquor is decanted and returned to the tank room. The first step in the treatment is the removal of the copper content, which may vary from 15 to 50 per cent. There are several methods of accomplishing this. The earlier method was to agitate the slime with a mixture of sulphuric acid and niter in a lead-lined vat by means of mechanically rotated paddles, heat being applied by means of steam coils in the bottom of the vat. The niter oxidized the copper, which was converted into copper sulphate. When the reaction was complete, the residue was washed and allowed to settle, and the liquor decanted and sent to the tank room. The mud was then filter pressed and sent to the refining furnaces. A modification of this process was in agitating the mixture by means of compressed air instead of the paddles.

The serious objection to the use of this method, aside from the expense of the niter used, was in the formation of large amounts of sodium sulphate, which went back to the tank room with the copper sulphate, and increased the resistance and specific gravity of the electrolyte. In order to avoid this and to do away with the expense of niter, the slimes were then given an air roasting after which they were boiled with acid to remove the copper sulphate. This method has almost entirely supplanted the former one.

The slime is either spread in thin layers in trays or in a thin layer on the hearth of a roasting furnace, and heated with a large excess of air to a point where oxidation occurs, but below the point where the slimes start to sinter. The slime may or may not be rabbled during the roasting, depending upon the existing facilities for catching the flue dust that is formed. When no rabbling is done, the time for the oxidation is necessarily of longer duration. When the roast is completed, the slime is removed from the roasting furnace and conveyed in cans to the boiling tank, where it is boiled with dilute sulphuric acid, which removes the oxidized copper as copper sulphate. It frequently occurs that in this boiling a considerable amount of silver goes into solution, and this must be precipitated by the addition of the necessary amount of raw slime, the metallic copper of which reacts with the silver. The objection to this procedure is that an excess of the raw slime is generally added so that the finished

slime contains more copper than is desired. A method of avoiding this was patented by Keller<sup>1</sup> and consisted in mixing the raw slime with just sufficient sulphuric acid to satisfy the copper present. The mixture is then charged into the roasting furnace and heated until the desired reaction is accomplished.

By any of the above methods the copper in the treated slime may be reduced to about 1 per cent, and the slime is then ready for the furnace treatment. The furnaces used are generally small, basic-lined reverberatories, or else small, basic-lined tilting furnaces, the latter being preferable on account of the smaller amount of precious metal tied up in the furnace linings, an item of no small importance. The furnaces may be fired by fuel oil, gas, or powdered coal.

The slime is charged into the furnace with a small amount of soda in order to thin out the slag formed on the melting down. The slime readily melts, and during the melting a very fusible thin slag is formed, which is drawn off as it is formed, so as to keep the surface of the slime from being blanketed and slowing down the melting. When the charge is completely molten, further additions of soda are made and the charge is oxidized by compressed air through iron pipes inserted under the surface of the charge. During this oxidation the great bulk of the impurities are removed and the charge gradually assumes a metallic aspect. When the soda slag will remove no further impurities, the metal is covered with niter and the oxidation continued. This procedure brings the bath up to a good grade of doré, 980 to 990 silver plus gold, and the metal is then ready for casting into doré anodes. The niter slags formed during the last operation are generally charged back into the furnace with the succeeding slimes, the soda slags being sent to the blast furnace for recovery of the silver and copper contents. In some plants the soda slags are returned to the anode furnaces, but this practice is not to be recommended, as the various impurities in the slag enter the anode to a considerable extent, thus making them circulate in the system and usually giving trouble with the solution of the anodes in the tanks.

The doré, which is the name given to the high-grade mixture of silver and gold, is then cast into anodes by the use of a hand ladle. The anodes vary in size at the various plants, depending upon the process for removing the silver. For the average electrolytic process the size will be approximately 12 by 6 by  $\frac{1}{2}$  in. The anodes are then sent to the parting plant, where the silver and gold are separated. For this purpose there are two well-established processes in use at the present time, the sulphuric acid and the electrolytic, described in Chapter XXVIII.

Should there be platinum or palladium present in the doré these metals will accompany the gold. The methods of extraction are chemical or electrolytic. In the former the gold mud is boiled with strong sulphuric acid and a small amount of nitric acid or niter, which dissolves practically all of these metals. The resulting solution is then passed over copper to precipitate the silver and the platinum and palladium. The resulting sludge is then dissolved in *aqua regia*, which dissolves the platinum and palladium but leaves the silver as silver chloride. From this solution the platinum and the palladium are recovered by the use of ammonium chloride and ignited to give a metallic sponge of a purity of 98 per cent or better.

**Metal Losses in Refining.**—The question of metal losses in the refining of copper, with its accompanying silver and gold, is one of great importance. The sources of losses are numerous, and vigilant attention is required to keep them within proper limits. The usual sources of losses taken in the order the material passes through the plant are as follows: weighing, sampling, assaying, anode slag, anode flue dust, cathode loss, wire-bar slag, wire-bar stack, weighing, slimes loss in silver process, gold in fine silver, silver in fine gold. There are also certain losses, such as solution and theft losses.

<sup>1</sup> U. S. Patent, 1110493.

In weighing, considerable loss may be experienced through lack of proper care of the scales, and careless handling of test weights. In the average plant these points are generally given careful attention. A usual source of error in weighing lies in the taring of the cars carrying the incoming blister. These should be carefully tared at stated intervals and particularly after any repair work has been done on the car, no matter how slight. An error of considerable magnitude may be caused in weighing cars that are not properly protected from the wind while on the scale.

Sampling errors may easily run into large figures, and every possible precaution should be taken to see that the best practice is in use. This is particularly important where the blister copper contains considerable silver and gold. The question of moisture in blister copper has but recently been given the attention it deserves. The average copper is very porous and will absorb up to 0.5 per cent of moisture while apparently quite dry on the surface. A frequent source of error against the refinery lies in the occluded moisture from quenching the copper as it comes from the molds at the converters. This may amount to as much as 0.25 per cent and can only be determined by carefully drying the copper at a temperature sufficient to drive off the moisture, but not sufficient to oxidize the copper. No standard equipment and practice exist among the various refineries at the present time and there is much room for improvement along these lines.

In assaying, errors frequently occur through the laboratory using methods that give consistently low results or consistently high results. Unless the splitting limits are quite close, so that such methods are brought to the front by the frequency of umpire assays, a serious error may be introduced.

Anode and wire-bar stack losses will, to a large extent, depend upon the nature of the material being treated in the furnace. The apparent magnitude is not large judging from bag-house tests, particularly where, as is almost always the case, waste-heat boilers are installed.

Anode and wire-bar slag losses may, and frequently do, amount to a considerable item. These slags will run in the neighborhood of 40 to 50 per cent copper and must be retreated in a blast furnace for the recovery of the copper. It is necessary to slag off the silica content, and, as the slag from the blast furnace will contain some copper, it is apparent that the more slag is made in the reverberatory furnaces the more slag will be made in the blast furnace with its accompanying copper loss. This loss is particularly serious in cases where the refinery slags are treated in a black-copper furnace, as in such a case the resulting slags are very much higher in copper with a correspondingly greater copper loss to the refinery.

Cathode losses constitute one of the largest items of silver and gold losses in the process. There is always a certain amount of anode slime floating in the electrolyte and, if the cathode is rough, a large amount of this may be caught and thus pass into the wire bars where it is lost. This loss may be controlled by careful supervision over the factors affecting the cathode deposit, such as proper refining of the anode, current density, rate of circulation, etc.

In the treatment of the anode slime in the silver building there is opportunity for great losses in the furnace gases. In former years these losses were of considerable magnitude and it is only with the recent installations of the Cottrell system that their real magnitude has been appreciated. At the present time with properly designed Cottrell apparatus the losses from the silver-refinery roaster and furnace gases have been reduced to a very low point, though, even with this safeguard, careful watch must be kept on every step in the process for unsuspected leaks that, in the course of a year, may amount to considerable.

In the production of fine silver there is always loss of gold due to the difficulty of keeping the gold mud completely out of the silver crystals. Similarly, the refined



gold always contains some silver. The partial cure for such losses is in proper care of the doré anode bags so that the loss is reduced to a minimum.

The amounts of the losses in cathodes, silver, and gold are kept continually before the management through the daily assays, so that any tendency to go wild should be promptly discovered and means taken for correction.

Losses by theft may amount to a large item, particularly if there is much small stuff such as copper scrap, scrap wire, etc. received. Such copper is easily carried out of the plant in dinner pails, clothing, etc., and a careful watch must be kept to keep this at a minimum. A thorough policy of prosecution when an employee is caught will go a great way to prevent similar occurrences in the future.

In general, it may be stated that in a well-conducted refinery the copper losses will average about 7 to 8 lb. per ton of cathodes produced. Silver and gold should break about even, provided the assays are uncorrected; if corrected, the silver loss will be about 2 per cent and the gold loss about 1 per cent of the contents of the anode, as these figures are the average corrections for the usual type of copper received by the refineries.

**Properties of Refined Copper.**—The melting point of pure copper is 1083°C., which may be slightly reduced by the presence of small amounts of cuprous oxide. The boiling point is in the neighborhood of 2310°C., but experimental difficulties have prevented a precise determination.

The latent heat of fusion is 43.3 cal. per gram, and its specific heat varies with the temperature. The Bureau of Standards gives the latest determination as:

$$C = 0.0917 \times 0.000048(t - 25),$$

where  $t$  is the absolute temperature.

The electrical conductivity of copper varies greatly, depending upon the presence of minute quantities of various impurities. The following tables compiled from various sources, together with experimental work by the writer, show in a general way what may be expected. It must be kept in mind, however, that the presence or absence of oxygen in the copper may greatly vary the results. When the impurity is in solid solution, its effect is generally much greater than if it is in some other form.

PER CENT	CONDUCTIVITY,		CONDUCTIVITY, PER CENT
	PER CENT	PER CENT	
<b>Aluminum:</b>		<b>Bismuth:</b>	
0.000.....	100.0	0.000.....	100.0
0.006.....	99.0	0.005.....	100.2
0.050.....	84.0	0.010.....	99.5
0.100.....	67.0	0.050.....	98.5
<b>Antimony:</b>		<b>Cadmium:</b>	
0.000.....	100.0	0.000.....	100.0
0.020.....	97.5	0.025.....	99.9
0.050.....	95.0	0.050.....	99.6
0.100.....	88.0	0.100.....	99.0
0.250.....	75.0	0.250.....	97.0
<b>Arsenic:</b>		0.500.....	96.0
0.000.....	100.0	<b>Lead:</b>	
0.005.....	98.5	0.000.....	100.0
0.010.....	95.5	0.050.....	99.5
0.050.....	85.0	0.100.....	99.0
0.100.....	75.0	0.300.....	98.5
0.200.....	60.5		
0.500.....	40.0		

PER CENT	CONDUCTIVITY, PER CENT	PER CENT	CONDUCTIVITY, PER CENT
Nickel:		Tellurium:	
0.000.....	100.0	0.000.....	100.0
0.005.....	99.0	0.010.....	100.0
0.010.....	98.5	0.025.....	99.0
0.100.....	93.0	0.050.....	99.0
0.400.....	75.0	0.100.....	98.5
1.000.....	55.0	Tin:	
Phosphorus:		0.000.....	100.0
0.000.....	100.0	0.050.....	98.0
0.005.....	100.5	0.100.....	93.0
0.020.....	96.0	0.500.....	75.0
0.070.....	60.0	Selenium:	
0.150.....	42.0	0.000.....	100.0
Silver:		0.010.....	99.0
0.000.....	100.0	0.050.....	98.5
0.100.....	99.8	0.100.....	98.0
0.500.....	97.5	Zinc:	
1.000.....	95.5	0.000.....	100.0
Sulphur:		0.050.....	98.5
0.000.....	100.0	0.100.....	96.5
0.050.....	99.5		
0.100.....	98.0		
0.250.....	97.0		

The effects of the various impurities on the mechanical properties of copper may be summarized as follows:

*Arsenic* toughens, hardens, and increases the tensile strength of copper when present up to at least 1.5 per cent. It will not impair the forging properties when added in amounts up to 0.5 per cent and invariably improves the forging properties of impure copper.

*Antimony* hardens and strengthens copper, though not to the same extent as arsenic. It is not detrimental in amounts up to 0.5 per cent if other impurities are absent and the proper amount of oxygen is present.

*Bismuth* has by far the most deleterious effect on copper of any impurity; 0.02 per cent makes copper red short, 0.05 per cent makes it cold short, and 0.1 per cent makes it very brittle. The injurious effects of bismuth may, to a certain extent, be counteracted by the presence of oxygen.

*Cobalt* is said to confer greater durability at high temperatures and toughens, hardens, and strengthens copper in the cold.

*Iron*, when present in amounts in excess of 1 per cent, makes copper hard and brittle.

*Lead* when present alone in copper reduces the strength, ductility, and toughness of copper, as the latter has no solvent power for lead. The latter, therefore, honeycombs the structure more or less uniformly and greatly weakens it above ordinary temperatures. In the presence of oxygen and arsenic lead may occur to some extent without ill effects. In the absence of oxygen and arsenic 0.1 per cent lead will make copper unworkable, but with oxygen and arsenic present this amount is claimed to make copper roll better.

*Nickel* in small amounts—a few tenths—imparts strength, toughness, and increased resistance to deformation at high temperatures. In Germany, copper containing a

small amount of nickel is preferred to arsenical copper for the manufacture of fire-box sheets.

*Oxygen* in commercial, impure wrought copper is essential where the metal has to withstand repetition of small stresses, exposure to atmosphere, influence of corrosive agents, etc. Its presence offsets the harmful effects of bismuth, lead, etc. Copper containing too much oxygen is cold short, and, if the oxygen is in great excess, the metal is also hot short.

*Silicon*, when added to copper in amounts up to 3.5 per cent, increases the hardness and assists in the production of sound castings. With 6 per cent silicon, copper is brittle. A small amount of silicon, 0.1 per cent, added to copper will increase the fluidity of molten copper so that castings free from blowholes can readily be produced.

*Silver* in copper benefits its mechanical properties and has no effect upon its hot-working properties.

*Sulphur* in copper forms a highly dangerous brittle constituent and is very detrimental to the mechanical working of copper. When present, its bad effects may, to a large degree, be counteracted by the addition of manganese or aluminum.

## CHAPTER XXVIII

### REFINING OF GOLD AND SILVER BULLION

BY ELLY J. WAGOR<sup>1</sup>

**Parting.**—Gold and silver are so intimately associated in all classes of bullion produced in either mining or metallurgical operations that refining processes must not only consider the elimination of the base metals present in the alloy, but also the “parting” or separation of the gold and silver. This separation is effected either by dry, wet, or electrolytic methods.

The dry method is based on the conversion of the silver in the alloy to a chloride or a sulphide, while the bullion is in a state of fusion. This principle finds application in the so-called Miller process, in which chlorine gas is passed through the molten metal, converting the silver and base metals into chlorides which pass off as fumes or are skimmed from the surface of the molten charge. The use of this method is, of course, restricted to bullion carrying limited amounts of silver.

The wet method depends upon the solubility of silver and the insolubility of gold in either nitric acid or in boiling, concentrated, sulphuric acid. In practice, the sulphuric acid-parting process has gradually superseded the older and more expensive nitric-parting process.

The electrolytic method is essentially a wet method, but is based on electrochemical rather than simple chemical reactions. Electrical energy is used to produce chemical changes by the passage of a current through an electrolyte. The Moeblus, Balbach and other silver-refining processes for refining bullion in which silver predominates in the alloy depend on the solubility of silver and the insolubility of gold at one electrode, and a deposition of silver at the other under current action in a nitric electrolyte. The only differences in these silver-refining methods are certain mechanical variations and arrangements in the equipment used. The application of electrolytic parting to bullion in which gold is the predominant metal is found in the Wohlwill process of gold refining based on the solubility of gold and the insolubility of silver at one electrode, and deposition of gold at the other, under current action in a chloride electrolyte.

In this general outline of methods used in the parting of gold-silver alloys, detailed consideration will first be given to the Miller process, or the refining of gold bullion by the use of chlorine gas.

**Miller Process of Chlorination.**—The equipment and the operation of a comparatively recent installation in the Royal Mint at Ottawa, Canada, are described by Messrs. Cleave and Bond.<sup>2</sup>

This plant operates sixteen chlorination, two tilting, and four ordinary furnaces. The chlorination furnaces are of fire clay, cylindrical in shape, with an inside diameter of 9 in. and a depth of 18 in. This battery of furnaces is connected with a large flue chamber provided with a spraying system for washing and cooling the fumes developed in the operation of chlorination. Provision is made for the recovery of values in the

water through which the fumes have passed in a series of filters and settling tanks. Chlorine gas is supplied from cylinders housed in a brick, leakproof closet. The gas is conducted through a heavy lead pipe extending along the top of the flue chamber with a branch leading to each furnace fitted with a valve for regulating the flow of gas to the different units.

Clay crucibles are used having a height of  $11\frac{1}{4}$  in. and a diameter at the top of  $5\frac{3}{4}$  in. tapering to  $3\frac{1}{4}$  in. at the bottom. These are provided with slotted covers to allow inserting and withdrawing the clay pipe stems, which are about 2 ft. in length and  $\frac{3}{16}$  in. in diameter. In the operation of chlorination, the clay crucibles are placed inside of graphite crucibles as a safeguard against leakage or breakage.

Bullion for treatment is first melted in a tilting furnace in charges of from 7,000 to 8,000 oz. After the chlorination equipment is brought to a red heat, 600 to 700 oz. of the molten bullion from the tilter are poured into each crucible, sufficient borax having been previously added to form a cover  $\frac{3}{4}$  in. in thickness. The pipe stems are forced to the bottom of the crucibles and held in position by clamps. The gas is turned on slowly at first and the flow is gradually increased to the maximum where no free chlorine is given off. The base metals are immediately attacked, and pass off in dense fumes, which are drawn into the chamber through the furnace flues.

After the base metals have been practically eliminated, chloride of silver is formed, which floats on the surface of the gold beneath the borax cover. When chlorination has been completed, determined by a brownish stain formed on a clay rod held in the fumes, the remaining silver chloride and other impurities are baled off. The gold is then cleaned up with bone ash and poured into a mold and the crucible is ready for another charge.

The time necessary for the completion of the operation depends, of course, on the amount of silver and base present in the bullion. Bullion containing 800 parts gold, 150 parts silver, and 50 parts base metal per 1,000 requires  $1\frac{3}{4}$  hr. for chlorination, and during this period it is necessary to bale off the silver chloride formed three times to prevent it from overflowing the crucible.

The chlorides baled off during the operation are remelted in a No. 45 graphite crucible, and sodium carbonate is slowly charged in on the top of the melt. This effects a partial reduction of the chloride to metallic silver, which, in settling to the bottom of the crucible, carries with it the gold contained in the chloride. The charge is allowed to cool sufficiently to solidify the metal, and the still molten chloride is poured into shallow molds. The silver containing the gold is cast into anodes and refined by the electrolytic Mochius process.

The chloride cakes are treated in a tank with boiling water to remove the base chlorides, and then placed in another tank in alternate layers with iron plates for reduction of the chloride to metallic silver. This silver will sometimes approximate a fineness of 999. The gold from this process will average 996.5. With a plant as outlined, it is possible to produce 250,000 oz. of refined gold in a 48-hr. week.

**Sulphuric Acid Parting.**—This process has been described in detail by Schnabel in his "Handbook of Metallurgy," by T. K. Rose in "The Metallurgy of Gold," and by others, and consists essentially in four operations as follows: (1) blending of the bullion to required fineness and preparation for parting operation; (2) dissolving of the silver by sulphuric acid; (3) treatment of the residues for gold; (4) recovery of the silver from sulphate solution.

**Blending of the Bullion.**—The bullion must be blended or mixed in such proportion that a melt of prescribed weight must contain certain definite proportions of gold, silver, and base metals. The make-up varies in different plants, ranging from  $2\frac{1}{8}$  to 4 parts of silver to 1 part of gold according to the amount of copper

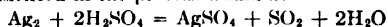
present. The sulphates of the base metals present in the bullion are only slightly soluble in concentrated sulphuric acid and care must be exercised in keeping the base-metal content within certain limits. The copper present should never exceed 10 per cent, and, if possible, should be kept under 6 per cent. Lead, up to 5 per cent, does not materially interfere with the process. The bullion is melted in graphite crucibles, in melts of from 3,600 to 6,000 troy oz.

In order to expose the maximum amount of surface to the action of the acid, these melts are either granulated or poured into thin slabs. Granulations are made by pouring the molten metal, in a small stream with a whirling motion, into large copper tanks filled with cold water. After pouring, the water is drawn off and the granulations are dried on heated trays of either copper or iron. Slabs for parting are cast into shallow iron molds  $\frac{3}{4}$  in. deep by 9 in. wide by 15 in. long. The advantage claimed for the slabs over granulations is in the less violent action of the acid, thus affording better control of the dissolving action.

**Solution of the Silver.**—This is effected in cast-iron pots of fine-grained, compact, white iron containing a small percentage of phosphorus or silicon. These pots are usually hemispherical in shape, 40 in. or less in diameter, with a  $1\frac{1}{2}$ - to 2-in. wall. Covers, either of cast iron or heavy sheet lead reinforced with iron, are fitted to the pots with lead-pipe connection for carrying off the fumes of sulphur dioxide and openings for charging with metal and acid. Dissolving kettles have capacities ranging from 3,600 to 16,000 troy oz.

For each part of silver in the bullion, 2 to  $2\frac{1}{2}$  parts by weight of commercial concentrated sulphuric acid, 66°Bé., are added. Heat to facilitate action of the acid is usually applied by wood fire and extreme care must be used in regulation of the temperature in controlling the ebullition. One-half of the total acid required is added at the start, and the remainder from time to time as the action warrants. During action, the charge must be stirred occasionally with an iron tool. The time required for complete solution of the silver varies from 6 to 12 hr., depending on the amount of base metal present and the care with which repeated stirrings are made. The acid vapors are led to a condensing chamber where particles of silver sulphate carried over may be deposited.  $\text{SO}_2$  may be recovered in leaden chambers as sulphuric acid, ferrous sulphate, or hyposulphite.

The reaction represented in the process would be



The base sulphates are only slightly soluble and, therefore, have a tendency to stay with the gold residues; their chemical reactions are, as a rule, quite complex. In the end a small amount of cold acid is added to help clear the solution. The clear solution of silver is ladled or siphoned into lead-lined tanks partly filled with hot water in which the precipitation of the silver is effected.

**Treatment of the Residues for Gold.**—Repeated boilings of the gold residues with fresh concentrated acid are necessary to remove the remaining silver and base metal. Often as many as seven boilings are necessary. Residues are finally washed with hot water or hot, dilute acid to remove the anhydrous sulphates. The gold is pressed, dried, and melted with a flux of niter and bone ash, and is cast into bars having an average fineness of 995.

**Recovery of Silver from Sulphate Solution.**—Silver may be recovered from solution by precipitation with copper, iron, or ferrous sulphate. The most common method is by copper replacement, in which the solution is brought to a



**Electrolytic Processes.**—Electrolytic methods of refining have, to a large extent, replaced or supplemented the acid-parting process not only in large-scale operations but also in the smaller plants, in private as well as government-operated refineries. The advantages over acid parting may be summed up as follows: (1) lower cost of operation; (2) higher standard of refined product; (3) neatness of operation and absence of noxious fumes; (4) recovery of the platinum metals as by-products.

The Moebius and Balbach systems of silver refining find application in the treatment of bullion ranging from a few points of gold, doré silver, up to 350 parts per 1,000; the Wohlwill process of gold refining, in the treatment of bullion containing 850 or better of gold per 1,000.



FIG. 1.—Moebius cells. Anode shown at left. Stripping cathode at right.

**The Moebius Process.**<sup>1</sup>—Wooden tanks of pitch pine may be used, thoroughly tarred to prevent leakage. These tanks, 2 ft. wide by 12 ft. long, are divided by transverse wooden partitions into seven compartments or units. In each compartment are suspended three rows of anodes and four rows of cathodes. The anodes are suspended in muslin bags or cloth frames which serve to collect the undissolved metals and prevent contamination of the deposited silver. The cathodes are thin, rolled strips of pure silver, which are straddled by mechanically operated wooden scrapers removing silver crystals as fast as they are deposited, and serving to keep the electrolyte uniform by gentle agitation. A removable tray is placed under the electrodes for removal of the silver, and all arrangements,

<sup>1</sup> For a description of this process as practiced at Maurer, N. J., see GRISWOLD, G. G., *Eng., Mining J.*, 107 (May 3, 1919) 789.



electrodes, scrapers, etc., in each unit are carried on a frame and can be lifted together from the refining tank.

The electrolyte is a weak solution of silver nitrate containing free nitric acid, though the operations may be started with a dilute solution of nitric acid.

In the treatment of doré silver bullion the permissible current density varies from 20 to 28 amp. per square foot of cathode surface and the potential across the electrodes, or of the unit, is from 1.4 to 1.5 volts. At this density about 40 per cent of the daily output of each unit is permanently held in stock in cathodes and electrolyte. The energy consumption is 13.2 watt-hr. per ounce of silver deposited.

The anode mud, consisting of gold, some silver, lead as peroxide, and other insoluble metals, is removed periodically from the bags, and, after washing, is parted by acid or other means.

The silver is deposited in a loose crystalline form easily removed from the cathode, although at lower current densities it is deposited in a more adherent form. An addition agent, as gelatin or glue in the electrolyte, to harden the deposit, is effective only when the solution is comparatively free from base metals.

**Balbach Process.**<sup>1</sup>—The electrolyte used in this process is the same as used in the Moebius, but the anodes, instead of being suspended vertically in the electrolyte, are placed horizontally in filter frames or baskets supported on the edges of the tanks, and the silver is deposited on a cathode fitted to the bottom of the refining cell or tank. Originally, this cathode was made of silver, but the universal practice now is to use graphite plates,  $\frac{1}{2}$  in. thick, cut to size to fit the bottom of the refining tank. Contact with these plates is effected by use of silver candle-shaped contact pieces cast in a special mold, and in a similar manner electrical connection is made with the anode. The anodes are cast in thin slabs and placed in the muslin-lined wooden frames or baskets with grill bottom. The insoluble residues accumulate on the under side of the slabs as the parting progresses, thus gradually increasing the resistance of the cell. The deposited silver is removed from the bottom of the cell by a long-handled scoop of wood or hard rubber; the anode basket being raised clear of the cell to facilitate the operation.

The distance between the electrodes is 4 in. and the depositing surface about 8 sq. ft. With a voltage of 3.8 per tank and a current density of 20 to 25 amp. per square foot, the energy consumption is 31.5 watt-hr. per ounce of silver produced and 32 per cent (approximately) of the daily output is held in process in electrolyte and contact pieces. No agitation or circulation of the electrolyte is required in this process.

A critical comparison of the Moebius and Balbach systems is made by F. D. Easterbrook.<sup>2</sup> It is to be noted that the Balbach cell is simpler in its operation, having no moving parts. Its energy consumption, however, is greater, and its depositing surface per unit of floor area is considerably less than that of the Moebius.

An innovation in silver refining has recently appeared in the Ottawa Mint, Canada, and is described by A. H. W. Cleave.<sup>3</sup>

The new cell makes use of a rotating cathode and permits of a current density of 150 amp. per square foot of cathode surface at a voltage of 2.5 without unduly increas-

<sup>1</sup> "Balbach Refining," *Elec. Chem. Ind.*, **2**, p. 302; THUM and EASTERBROOK, *Electro. Chem. Met. Ind.*, **6**.

<sup>2</sup> *Trans. Am. Electrochem. Soc.*, **8**, 125.

<sup>3</sup> *Eng. Mining J.-Press*, **116**, 21.

ing the temperature of the electrolyte. These cells are 36 in. in diameter and the electrolyte is contained in the annular space 8 in. wide by 18 in. deep between the outer and inner walls of the cell. The cathode carrier is supported at the center of the cell and is revolved by a shaft passing through this central hollow space. The deposited silver is loosely adherent and is automatically scraped from the cathodes, falling into removable trays from which the silver is removed every 4 hr.

An interesting comparison between the Moebius and new type of cell is given by Cleave.<sup>1</sup>

	Old cell	New cell
Amount of electrolyte in cell. . . . .	71 imp. gal.	52 imp. gal.
Weight of cathodes in use. . . . .	285 oz. (renewable every 3 weeks)	311 oz. (no renewals required)
Anodes in use . . . . .	5,104 oz.	2,310 oz.
Current consumption . . . . .	1.2 volts (350 amp.)	1.2 volts (400 amp.)
Current density per square foot, cathode surface. . . . .	13 amp.	75 amp.
Efficiency . . . . .	38 per cent	78 per cent
Labor required . . . . .	Stripping cathodes twice daily	No stripping required
Condition of electrolyte . . . . .	Continually gaining in strength	Constant
Agitation of electrolyte . . . . .	By mechanically driven stirrers (not thorough)	By rotation of cathode (thorough)
Output of silver per cell per hour	17.30 oz.	40.30 oz.

The United States government in its Mint and Assay Service operates three electrolytic refineries. All classes of bullion are received for refining, except that in which the base-metal content exceeds 800 parts per 1,000, and electrolytic processes are used exclusively in the parting and refining operations, the Moebius and Balbach-Thum processes for silver, and the Wohlwill method for gold. Most of the refined silver is produced by the Moebius or "vertical system," the Balbach-Thum or "flat cells" being used to supplement the Moebius-cell operation in treatment of the unparted anode remnants and bullion too base to be handled by the "vertical system."

The cells used in the "vertical system" are of vitrified, acid-proof stoneware, either of brown earthenware or domestic porcelain, 44 in. long, 24 in. wide, and from 18 to 24 in. deep. The electrode supports are either hard-rubber rods reinforced by a steel core, or close-grained maple sticks, rounded on one side and painted with an acidproof paint. Half-round conducting strips of either gold or silver cover the top sides of the electrode supports and are fastened to bus bars placed along the edge of the cells. The distance between electrodes varies from 2½ to 3 in. The anodes are cast with a hole in the top and are suspended in muslin bags from the conducting supports by C-shaped hooks of gold. The cathodes are strips of silver rolled out to a thickness of ⅓ in. and bent over at one end to hang from the supports.

<sup>1</sup> *Loc. cit.*

The electrolyte is a 3 per cent solution of silver nitrate containing about 2 per cent of free nitric acid. It is kept uniform either by circulation effected by air lifts of hard rubber, forcing the solution from the bottom of the cell and discharging at the surface, or by gentle agitation furnished by glass propellers connected to a motor-driven line shaft.

The first step in the operation is the preparation of the bullion for refining; the making of anodes for the refining cells. While the process allows considerable latitude in the amount of gold in the anode, it is customary in practice, in order to secure more uniform conditions in the cells, to make up anodes having a definite ratio of gold to silver. The usual make-up is an alloy containing 300 to 350 parts of gold per 1,000 with not over 100 to 150 parts of base produced by blending low-grade gold bullion, which cannot be handled directly by the Wohlwill process, with bullion in which the silver predominates. These silver anode melts of from 4,500 to 4,800 troy oz. are melted in No. 100 graphite crucibles and cast into anodes of the desired shape and size. A tapering pin in the mold provides the hole in the anode used for suspension in the cell.

A current density of 14 amp. per square foot of cathode surface is maintained, using a voltage of from 1 to 1.3. Under current action, the silver and base metals are dissolved at the anode, the gold and insoluble residues remaining in the muslin bag in a brittle brownish-black condition resembling a poor grade of lignite. This "black gold," as it is called, retains the original shape of the anode, and when removed from the cells it is broken up to remove "cores" of unparted bullion which it sometimes contains. After a thorough washing with hot water the black gold is dried and melted into anodes for treatment by the Wohlwill process. The fineness of these anodes depends not only on the quality of silver anodes from which obtained, but also on the current density used in the parting operation and the condition of the electrolyte. The fineness ranges from 800 to 900 parts of gold with 80 to 100 parts of silver.

Pure silver is deposited on the cathodes in a crystalline form which is scraped from the cathodes at intervals into porcelain jars. Crystals which fall to the bottom of the refining cells are periodically removed and added to the cathode production. The collected silver is thoroughly washed with hot water, either in porcelain filters or earthenware centrifugal machines. In the latter case, the silver is placed, in an earthenware basket or rotor, lined with 7-oz. cotton duck, provided with a series of channels at its periphery for carrying off the wash water. This basket makes 800 r.p.m. and washing is effected very rapidly. After washing, the centrifugal is operated for a time, drying the silver sufficiently to be removed and charged into the crucible for melting. If washing is done in an ordinary filter, provision is made for drying the silver crystals in a steam drying oven. The silver is melted in No. 100 to 125 graphite crucibles in melts of 5,000 to 5,500 troy oz. without the use of fluxes, and cast into bars having an average fineness of 999.5. A cast-iron cover, placed over the mold after pouring, prevents "spitting" of the silver in cooling.

There is a gradual depletion of silver and acid in the electrolyte as the base metals pass into solution at the anode, and this must be taken care of by additions of strong silver nitrate and nitric acid. The electrolyte is tested at intervals to determine the extent of this depletion. Titrations are made with potassium thiocyanate, using ferric sulphate as an indicator for silver determinations, the acid being determined by potassium hydroxide, with methyl orange as an indicator.

The "flat cells" of the Balbach-Thum process, used to work up the cores or unparted remnants of the bullion from the vertical cells, are of brown earthenware, 39 in. long, 19 in. wide, and 12 in. deep. The tray or basket, in which is placed the unrefined bullion, is either of earthenware or of wood. If wooden baskets are used, no metal should be used in their construction. Several thicknesses of filter cloth are

needed in the basket, as the parting is attended with considerable heat. Connection is made to the anode by a candle made up of a 50 per cent gold and 50 per cent silver alloy, which easily withstands the action of the current, and to the carbon plates or cathodes by long candles of fine silver. Copper lugs are fastened to the tops of these candles for connection with the conducting cables. The distance between electrodes is about 6 in. and the depositing surface is 5 sq. ft. The resistance of this cell is high, requiring a potential of 5 volts to maintain a current density of 14 amp. per square foot. No agitation or circulation of the electrolyte is needed.

The operation of these cells is similar to that in the vertical cells. The silver is removed by long-handled scoops of rubber or wood and added to the production of the other process, and the "black gold" from the baskets is washed and melted into anodes for the gold cells. Three or four of these cells will take care of the cores from sixteen vertical cells.



FIG. 2.—Wohlwill cells with glass-propellor agitation (foreground); Moebius cells (center); Thum-Balbach cells with candle connections (right).

The electrolyte becomes foul in time and is drawn off, and the silver in this solution, together with the wash waters from the fine silver and black gold, are recovered by precipitation on copper scrap as cement silver. This recovered silver may be used in the making of strong silver nitrate for additions to the refining cells or in the make-up of silver anodes.

A flow sheet of the silver-refining process (Fig. 1) outlines the general procedure in the government refineries.

**Wohlwill Process of Gold Refining.**—The cells are of white Royal Berlin porcelain, 16 in. long by  $11\frac{1}{2}$  in. wide by 12 in. deep, inside, usually arranged in batteries of twelve to fifteen cells connected in series. One plant is successfully using cells of domestic porcelain 44 in. long, 24 in. wide, and 18 in. deep. Electrode supports are of porcelain or hard-rubber, steel-reinforced rods, or, where the larger cells are used, maple sticks painted with acidproof preparation are used. As in the silver system, these supports are covered with strips of gold for conducting the current. The anodes are cast with a hole in the top and suspended

from the anode supports by C-shaped gold hangers or hooks. They are cast in a shape to minimize the amount of scrap to be retreated as shown in the accompanying illustration.

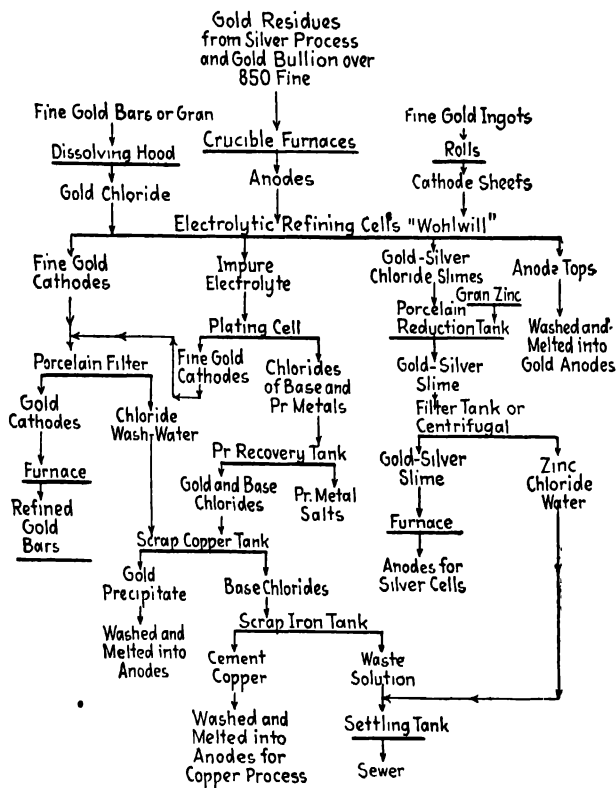


DIAGRAM 2.—Gold refinery flow sheet.

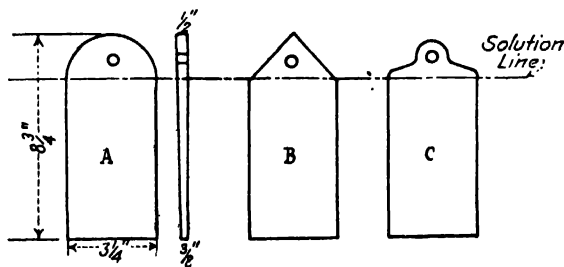


FIG. 3.—Anode types.

While anode *C* seems to offer the smallest percentage of scrap for remelting, a larger percentage of the anodes were broken when casting, as the metal is often quite brittle. At best, about 10 per cent of the metal treated in the cells is returned for remelting in the form of anode tops. The tapering of the anode in its thickness

permits of more uniform corrosion in the cell; the strongest action being at the solution line.

The cathodes are strips of fine gold rolled out to a thickness of 0.01 in. and cut to proper length. One end is turned over to permit of hanging from the cathode support. These starting sheets are annealed to prevent warping or buckling in the cell, care being used not to soften the turnover which supports the weight of the deposited gold.

The electrolyte is a solution of gold chloride containing 50 to 60 g. to the liter of gold, with 5 to 7 per cent of free hydrochloric acid. It is kept uniform in the same manner as the silver cells, either by circulation, using an air pump, or agitation furnished by glass propellers.

The current used is a pulsating or non-symmetrical alternating one, obtained by connecting a direct-current generator in series with an alternating-current source, which source may be either an alternating-current generator of proper voltage, or a high-voltage source stepped down by use of an induction regulator. The refining can be done by direct current alone, but the pulsating current makes possible the refining of gold bullion containing a higher percentage of silver at higher current densities and with less free acid. This current, its application and advantages, are described by the inventor, Dr. Emil Wohlwill.<sup>1</sup>

In each cell there are three anode and four cathode supports. Three cathodes are suspended from each support, giving a total depositing surface of 2.8 sq. ft. per cell. The depositing surface in the large cells mentioned is 10 sq. ft. The current density used is from 50 to 70 amp. per square foot of cathode surface, and the ratio of alternating to direct current is determined by the silver content of the anode.

Under current action, the anodes which contain from 8 to 10 per cent of silver are dissolved, the gold as well as the platinum metals together with the base passing into solution, while the silver is changed to insoluble chloride and falls to the bottom of the cells. Osmiridium crystals in the anode are not affected by the current and fall with the silver chloride. An excess of silver in the anodes forms a coating of chloride, which protects them from further action, thus rendering them practically insoluble, and an evolution of chlorine results.

The gold deposited at the cathode is very hard and quite dense and the starting sheet is melted with the deposited gold. The cathodes are removed after receiving a deposit of from 150 to 200 oz. of gold, washed in porcelain filters, dried, and melted without the use of fluxes in melts of 8,000 to 9,000 oz. and cast into bars having an average fineness of 999.5 to 999.8. Frequently, these melts will run to 999.9 in fineness.

As the base metals are dissolved at the anode the gold content of the electrolyte drops and it is necessary to add strong gold chloride at intervals. A rapid and fairly accurate method of testing the electrolyte is to precipitate the gold in 1 c.c. with an excess of ferrous ammonium sulphate, and to determine the excess used by titrating back with potassium permanganate. The ferrous solution is prepared by dissolving 154 g. of the salt in 500 c.c. of distilled water, adding 5 c.c. of concentrated sulphuric acid and diluting to 1 l.; 1 c.c. of this solution will precipitate 25 mg. of gold. The permanganate solution is made up so that 1 c.c. will equal 1 c.c. of the ferrous solution by dissolving 12.3 g. of the salt in 1 l. of distilled water.

In order to take care of the depletion of gold in the electrolyte, it is necessary to keep constantly on hand a stock of strong gold chloride. This chloride is made either by dissolving fine gold bars or granulations in *aqua regia*, or electrolytically, by passing a current through an electrolyte of concentrated hydrochloric acid, using anodes of fine gold and fine gold cathodes suspended in a porous porcelain cell. The porous cup prevents the deposition of the gold at the cathode and the gold dissolved at the anode is retained in solution. In either method the operation is carried on

<sup>1</sup> *Met. Chem. Eng.*, 8 (February, 1910)



FIG. 4.—Motor-driven earthenware centrifugal for washing and drying slimes.



FIG. 5.—Wohlwill cells. Anode shown on left, cathode on right, thin rolled gold strips in foreground for starting sheets.

under a hood. The resultant gold chloride has a strength of 375 to 450 g. of gold per liter.

About 5 per cent of the gold treated falls mechanically into the silver chloride slimes. The reduction of the silver chloride is effected by use of granulated zinc in porcelain tanks, sufficient acid being present to start the action. After reduction is complete, the slimes are thoroughly washed in a filter or centrifugal machine and melted directly into anodes for the silver-refining cells. These slimes will average in fineness from 250 to 500 parts gold, 30 to 40 parts base, balance silver, and in the melting, sufficient gold or silver bullion is added as required to produce an alloy of the fineness required by the silver-refining operations.

The gold in the spent electrolyte and wash waters is recovered by precipitation with ferrous sulphate or by scrap copper. As gold so recovered is in a very fine state of division and difficult to melt and wash without loss, an electrolytic recovery is to be preferred. This is accomplished by the use of a double-compartment cell in which a small cell is placed in the center of a large cell. The inner cell is charged with concentrated hydrochloric acid, while the foul electrolyte is placed in the outer cell, and connection is made between the two solutions by a series of short, glass siphons resting on the edge of the inner cell. The air is exhausted from these siphons and the solutions enter, thus permitting a flow of current through the electrolyte. Anodes of fine gold are suspended in the inner cell and gold strips in the outer cell. Under current action, gold chloride is formed in the inner compartment and the gold in the spent electrolyte is deposited on the cathodes. By regulation of the voltage, practically all the gold in the foul electrolyte may be plated out and the gold so obtained forms parts of the regular production of the cells. One or two of these plating cells will handle all the foul electrolyte from forty-eight of the small refining cells and at the same time add considerably to the stock of strong gold chloride.

As the government has no interest charges to consider, on metal held in process, the noble metals are used for conductors, and the problem of securing good electrical contacts is in a measure eliminated.

A flow sheet (Fig. 2) shows the procedure in gold-refining operations.

All the foul solution from which the silver and gold have been recovered is pumped into large wooden tanks containing scrap iron, in which the copper is recovered as cement copper, and any gold, silver, or platinum metals which have escaped the previous operations are recovered. To recover the values in this cement copper, a small electrolytic copper plant is operated, producing pure copper and a sludge containing the precious metals. This sludge is a veritable drag net of impurities, containing besides Au, Ag, and Pt, the base metals Cu, As, Sb, Pb, Bi, etc. This is usually handled in small amounts in silver-anode melts and the precious metals recovered from the regular process.

**Platinum Recovery.**—To the spent electrolyte from the gold-refining cells is added a saturated solution of ammonium chloride, which precipitates incompletely the platinum as the yellow double salt, platinum-ammonium chloride, together with salts of iridium and other platinum metals. This precipitate is allowed to settle and the solution is siphoned into a tank and electrolyzed, using insoluble carbon anodes and gold cathodes. An evolution of chlorine at the anode forms with palladium the red double salt, which falls to the bottom of the tank, and gold is deposited at the cathode. This method of palladium recovery is not used, however, when the gold has been removed by methods previously mentioned.

These first precipitations of platinum and palladium contain 15 to 20 per cent of impurities. They are washed with a solution of ammonium chloride, dried, and



reduced to metallic sponge by gentle heating. Purification of the sponge is accomplished by redissolving and reprecipitating. The usual procedure in refining platinum sponge is to use *aqua regia* as the solvent and to evaporate the solution to dryness to expel the nitric acid and reprecipitate the platinum with ammonium chloride. In large-scale operations this is a very tedious method, and in the government refineries solution of the crude or impure sponge is effected electrolytically as follows:

The crude sponge is placed in perforated stoneware cells holding about 250 oz. which are suspended in an electrolyte of hydrochloric acid and serve as the anodes. The cathodes are platinum strips suspended in porous porcelain cells, to which has been added hydrochloric acid. The action is similar to that of the cell previously described for the manufacture of gold chloride, the platinum being dissolved at the anode and the porous cup preventing the deposition of the dissolved platinum. This platinum solution is filtered and the platinum precipitated in the usual manner with ammonium chloride, which yields a sponge having a purity of 99 per cent or better. As the precipitation of platinum from its solutions is rarely complete, the filtrates and wash waters are treated with metallic zinc for the recovery of the remaining values.

The purification of the red salt of palladium is effected by first washing with ammonium chloride, dissolving in ammonium hydroxide, filtering, and reprecipitating as the yellow salt by cautiously adding hydrochloric acid to the ammoniacal solution. This yellow salt is redissolved and reprecipitated as above, yielding a sponge after washing and reduction, 99 per cent or better.

An excellent treatise on the metallurgy of platinum is given by Louis Duparc,<sup>1</sup> which has been translated by Redding and Nelson.<sup>2</sup>

<sup>1</sup> DUPARC, LOUIS, "Le Platine Du Monde," Chap. XV.

<sup>2</sup> Report of State Mineralogist of California, 28 (April, 1922).

## CHAPTER XXIX

### HYDROMETALLURGY OF GOLD AND SILVER

By W. J. SHARWOOD<sup>1</sup>

**Occurrence of Gold.**—Native gold is invariably alloyed with more or less silver, but it is exceptional to find any other metal in the alloy. It is found in veins associated with quartz and various sulphides—notably pyrite, pyrrhotite, galena, chalcopyrite, arsenopyrite, less commonly blende; sometimes with carbonates, especially ankerite; and small proportions of tellurides of lead and bismuth. Sometimes the metal is finely disseminated through such sulphides, sometimes deposited on the surface of the mineral particles in fairly large grains. One particular sulphide, *e.g.*, chalcopyrite, may monopolize the gold. In the oxidized portions of veins the gold is often associated with limonite, and gold-bearing quartz often contains small proportions of copper carbonates and manganese oxides. Electrum, containing 35 per cent or more of silver, is found only in the vicinity of silver mines. When gold is found apparently disseminated in igneous or metamorphic rocks, minute veinlets of quartz or carbonate usually accompany it.

Gold telluride, usually containing silver and sometimes mercury telluride, occurs in veins of quartz and carbonate; when oxidized, the resulting native gold is often extremely pure and finely divided, and may be coated with tellurous oxide (mustard gold).

The gold of placers or creek and river gravels is found occasionally in nuggets of large size, but more commonly in small grains, often water worn; in some deposits a considerable proportion of the grains pass a 200-mesh sieve. The silver content averages less than in vein gold, and it is, as a rule, easy to amalgamate. That from buried river gravels is similar, but often coated with oxide or sulphide of iron. The gold of sea beaches is usually finely divided or in thin scales.

For metallurgical purposes gold has been roughly classified as “free” or amalgamable and “refractory;” “float gold” is fine and in a condition making it easily floatable on water—the telluride is also easily floated—“rusty gold” is coated with some mineral which retards amalgamation (usually oxide of iron, manganese or tellurium); “encased gold” is completely enveloped in grains of quartz or other mineral and requires finer crushing to liberate it.

Among the minerals sometimes mistaken for gold may be mentioned pyrite and marcasite, and especially chalcopyrite. Grains of the latter, in polished faces of ore, often closely resemble gold in color and luster. Thin flakes of biotite and other micas, especially when partly oxidized, and other micaceous minerals, such as hematite and limonite, may also imitate it closely.

In panning or concentrating, many people have been misled by heavy lead minerals of a yellow color, such as the molybdate, chromate, tungstate, and even the phosphate,

<sup>1</sup> Lead, South Dakota.

but these are distinguishable under a lens or low-power microscope by their brittleness and transparency. Some of the numerous basic sulphates of iron are at times difficult to distinguish from gold when exposed on freshly fractured vein stuff. Particles of natural or artificial litharge, brass, or "spelter solder," and even superficially oxidized lead alloys, sometimes bear an astonishing resemblance to gold. These, and specks of native copper or copper from blasting caps, may find their way into mine samples or drillings and be found in panning.

On the other hand, mustard gold, resulting from oxidation of telluride, may have a distinctly earthy luster, and gold of low fineness may be easily overlooked.

Native silver and the chloride characterize the oxidized zone of most deposits. Native silver, usually nearly pure, occurs in very fine particles, threads, etc., and sometimes in masses which may reach several thousand pounds weight. In the Michigan copper mines pure silver and pure copper occur attached and intergrown. Some native silver contains a little mercury. Coarse lumps are best hand picked, but the smaller are concentrated, or amalgamated, and the fines cyanided.

The chloride ( $\text{AgCl}$ ), is readily reduced to metal by contact with metallic Fe, Zn, Al, or even Cu in contact with an electrolyte, and is then easily amalgamated by mercury. Alkaline cyanide, or thiosulphate solution, dissolves it readily, and also silver bromide and iodide which often accompany it; strong solutions of chlorides have less solvent action.

The sulphide ( $\text{Ag}_2\text{S}$ ), dissolves in strong cyanide solution, but not in chlorides or thiosulphates. It is slowly amalgamated by mercury when in contact with an electrolyte, and the action is facilitated by thiosulphates and copper salts, and especially in the presence of metallic iron, etc. When roasted it yields  $\text{Ag}_2\text{SO}_4$ , which is somewhat soluble in water.

The numerous complex sulphur-arsenic and sulphur-antimony compounds of silver are not so readily amalgamated unless roasted; they are decomposed by grinding with metallic aluminum and sodium hydroxide or carbonate.

Galena often contains silver in the form of sulphide; and the selenide ( $\text{Ag}_2\text{Se}$ ) and occasionally the telluride ( $\text{Ag}_2\text{Te}$ ) occur in small amounts in some gold and silver ores, and apparently in some copper deposits.

**Gold and Silver Alloys.**—Pure gold is distinctly softer than silver; either is hardened by the addition of a small proportion of the other, or of copper or other base metal. In gold-silver alloys the maximum hardness occurs with about one-third silver. Small additions of silver reduce the gold color materially, but affect the melting point very little up to about one-third silver. Electrum is gold, especially the native metal, containing 15 to 45 per cent silver, rendering it pale. Green gold is a similar alloy containing about 10 per cent silver. The red-gold alloys contain copper.

Jewelers' gold usually ranges from 18 (Au 750) to 10 k. (Au 416) and frequently contains both copper and silver as alloy.<sup>1</sup> The lower grades often contain some zinc, which helps to counteract the redness due to copper. They are sometimes made by alloying brass with gold, but extreme care is necessary to avoid certain impurities in the brass or copper used, especially lead or arsenic, which cause brittleness. British gold coin is 22 k. (Au 916.6), but alloys as low as 9 k. (Au 375) are recognized and hall marked in England.

White gold is properly an alloy of gold with palladium; if legitimately stamped 18 k., it will contain 18 parts gold (Au 750) and the remaining 6 parts are palladium, with usually a little silver. This alloy has a pure-white color and a high melting point.

<sup>1</sup> See p. 39, "Metallography," this book.

Palau and rhotanium are similar. A cheap imitation is produced by melting gold with a nickel alloy. The mixture sold for producing "white gold" by adding it to fine gold is: Cu, 55 per cent; Zn, 21 per cent; and Ni, 24 per cent. A similar mixture for producing "green gold" is merely brass: Cu, 67 per cent; and Zn, 33 per cent.

For soldering gold there are many recipes, the aim being to produce an alloy considerably more fusible than that of which the object is made, but not differing much in color. Many of these soldering alloys contain a considerable proportion of zinc with copper, silver, and gold; when associated with copper, several per cent of zinc do not cause brittleness, though the alloys are often extremely hard and difficult to roll. In recent formulas cadmium is substituted for zinc. Such solders lose zinc (or cadmium) by volatilization when heated, becoming gradually less fusible.

Aluminum forms a number of alloys with gold, one of these (AuAl<sub>3</sub>, 22 per cent Al) has a remarkable purple color. The so-called aluminum gold is an alloy of copper with about 25 per cent Al, very slightly attacked by nitric acid, and closely resembling gold in color, but of low specific gravity.

**Pure silver** when melted, absorbs oxygen from the air (up to twenty-two times its own volume) unless air is displaced by some other gas or the fused metal covered with borax, salt, or charcoal. On cooling to near solidification this oxygen is given off suddenly, the surface of metal sprouting or spitting. Small proportions of foreign metals usually prevent this. The oxygen is probably retained by fused metal as a suboxide, like that held by copper after solidification. Gold does not absorb oxygen.

When gold or silver containing a small percentage of lead is heated, or is kept just below solidifying point, a eutectic rich in lead exudes or liquates out; this often oxidizes, producing a peculiar "vegetation" on the surface. This is due to formation of PbO mixed with minute globules of gold (or silver). In extreme cases the entire alloy may form a soft, cauliflower-like mass.

The small proportion of silver alloyed with native gold and mill bullion is of some economic importance, usually more than covering cost of marketing refined bars. Assuming silver at 50 cts. per ounce, the per cent of gross value due to silver is as follows:

Ratio		Percentage, silver value
Gold	Silver	
900	100	0.27
800	200	0.60
700	300	1.03
600	400	1.60
500	500	2.35

With silver at \$1 per ounce, these figures would be nearly doubled, and for other values nearly proportional.

A minute proportion of lead—less than 1 part in 1,000—makes gold brittle, especially when hot. This seems to be due to a highly fusible eutectic, which can be seen between the crystals of pure metal in a polished and etched section. Similar effects

are produced by Bi, Te, Sn, Sb, As; while Zn and Cd in fair proportions yield less brittle alloys. Annealing removes brittleness due to traces of Pb, not that due to Bi or Te. Silver is similarly affected by most of these elements.

Tellurium renders gold extremely fusible; on heating in air the tellurium is slowly volatilized or oxidized, leaving bright globules of gold still retaining some tellurium.

Gold combines or alloys readily with tellurium, and with fusible metals generally, forming fusible alloys, it is not attacked by the vapor of selenium or sulphur. Silver is at once attacked when heated in the vapor of S, Se, or Te, forming  $\text{Ag}_2\text{S}$ ,  $\text{Ag}_2\text{Se}$ , or  $\text{Ag}_2\text{Te}$ ; like gold it alloys readily with fusible metals.

Gold resists all single acids, but is readily attacked by *aqua regia*; the most effective proportions are 1 part of nitric to about 4 parts of strong hydrochloric acid; any mixture of hydrochloric acid with a nitrate, nitric acid with a soluble chloride, or sulphuric acid with a nitrate and a chloride similarly attack it. It is very slowly acted upon by hot solution of ferric chloride. Moist chlorine gas converts gold into  $\text{AuCl}_3$ . Silver combines superficially with Cl, the  $\text{AgCl}$  then protecting the metal unless removed by some solvent. For this reason Au-Ag alloys are not dissolved completely by *aqua regia* unless the  $\text{AgCl}$  is removed from time to time from the surface by scouring or by some solvent, such as ammonia, cyanide, or hyposulphite.

Gold-chloride solutions ( $\text{AuCl}_3$ ,  $\text{HAuCl}_4$ ,  $\text{NaAuCl}_4$ , and other chloraurates) are reduced to metal if evaporated and gently heated, and are also reduced to metal by nearly all reducing agents such as base metals generally,  $\text{SO}_2$  and salts of  $\text{Fe}''$  and  $\text{Sn}''$ . Silver is readily dissolved by nitric or hot sulphuric acid, NO or  $\text{SO}_2$  being evolved, but resists most others. Silver nitrate, sulphate, and chloride are not readily decomposed but may be heated without decomposition; they are easily reduced to metal by contact with base metals, Zn, Fe, Cu, etc.

**Parting.**—The cupellation of lead removes it as oxide, together with other base metals, leaving gold and silver. Silver-bearing lead may be enriched by the Pattinson process, in which crystals of pure lead are removed, leaving the more fusible eutectic, the process being carried on in stages and the enriched lead finally cupelled. Silver and gold may be more readily removed from lead by the Parkes process, in which a small percentage of zinc is added which, on cooling, crystallizes and rises (zinc being insoluble in solid lead), carrying up the precious metals as a crust, which is removed and refined.<sup>1</sup>

Gold and silver are separated or parted by means of nitric acid, NO being given off and  $\text{AgNO}_3$  formed. This requires the ratio Ag: Au to be at least 2:1, though 3:1 was formerly preferred. Hot sulphuric acid also dissolves silver away from gold if the proportion of silver is large enough,  $\text{SO}_2$  being evolved. Gold containing relatively little silver must have silver (or in some cases base metal may be used) added to reduce the gold to such a proportion that it will not protect the silver from attack.

It is preferable to use the Wohlwill process, electrolyzing the gold in a solution of  $\text{HAuCl}_4 + \text{HCl}$ , with gold cathodes, an alternating current being sometimes superposed upon the high density direct current used. Silver remains insoluble as  $\text{AgCl}$ .

Silver containing but little gold is electrolyzed in a slightly acid solution of silver nitrate, with a silver or carbon cathode, leaving gold insoluble; this is used in the Moebius, and Balbach-Thum processes.

The following tabulated data are of value in connection with the refining of gold and silver:

<sup>1</sup> See pp. 911 to 917, this book.

	Gold	Silver	Copper
Melting point, degrees Centigrade. . . . .	1063	961	1083
Specific gravity. . . . .	19.3	10.5	8.95
Specific volume (cubic centimeters per gram). . . . .	0.0518	0.0952	0.1117
Cubic inches for 1,000 troy oz. = 1,898/sp. gr. . . . .	98.3	180.8	212
Cubic inches for 100 lb. avoird. = 2,770/sp. gr. . . . .	143.5	263.8	309.5

In an alloy containing  $G$  per cent gold,  $C$  per cent Cu, and  $S$  per cent Ag, the specific gravity is very closely

$$100 \\ 0.0518G + 0.0952S + 0.1117C$$

Cementation is an ancient method of freeing gold from silver and base metals. The metal was first granulated by pouring into water, or beaten into thin plates. It was then placed in crucibles with a large proportion of aluminous earth and heated; silver, etc., was slowly oxidized (or possibly converted into sulphate or sulphide) and absorbed. Most recipes, however, include common salt and burned clay or powdered brick, tile, etc. When heated in contact with these, silver chloride is formed, fused, and absorbed. Gold treated several times in this way ("seven times tried in the fire") was rendered nearly pure.

Sulphur or pyrite was also used; heated in sulphur vapor, most of the silver and copper form  $\text{Ag}_2\text{S}$  and  $\text{Cu}_2\text{S}$ , which can be mechanically removed.

In *Guss and Fluss* parting, an alloy, containing at least 50 per cent gold, was heated in a crucible with 3 parts antimony sulphide, and poured into a mold; the gold, alloyed with antimony, etc., is found at the bottom and easily separated from the layer of "plachmal" above it. This gold alloy was then fused with 2 parts of antimony sulphide, and the product again with 1 part. The process was repeated if necessary until enough silver had been removed, when the gold was finally melted with borax and the alloyed antimony oxidized by a blast of air.

In the sulphur-litharge process (*Pfannenschmied*) a granulated alloy, rich in silver, was heated with sulphur, yielding  $\text{Ag}_2\text{S}$ , in which gold is disseminated. To collect the gold, a small percentage of litharge was added, yielding a fusible lead-silver alloy, which carried down most of the gold; a second or third treatment removed practically all the gold. Metallic iron was sometimes used instead of litharge to reduce a portion of the silver and collect the gold. Reduction of the remaining sulphide yielded a fairly pure silver.

Gold bullion, rendered brittle by Te, Bi, Pb, etc., may be softened by throwing a little  $\text{HgCl}_2$  on the fused metal, also by adding solid  $\text{AgCl}$  or  $\text{Ag}_2\text{SO}_4$ , by stirring with Cl gas or an air blast; stirring with  $\text{NaHSO}_4$ ,  $\text{NaNO}_3$ , or  $\text{MnO}_2$  is also effective. More or less silver may be removed by these methods, especially by Cl or  $\text{NaHSO}_4$ .

**Recovery of Gold and Silver.**—All gold and silver ores yield a high percentage of their precious metal when smelted with lead or copper ores, and an almost complete saving of them is effected in refining the lead and copper recovered. A large proportion of the silver of the world, and a considerable amount of the gold, is thus obtained as a virtual by-product from the smelting and refining of lead and copper ores, including some zinc-lead and zinc-copper ore. Some of this precious metal comes from concentrate, some from siliceous ore used as flux; comparatively

little true gold or silver ore is directly sold for smelting. Smelting charges and deductions on the full weight of ore, with the cost of freight and loading, often make it advisable to adopt some method which may be far inferior metallurgically, as regards percentage recovery, but which puts the precious metal in a form in which it is more readily salable, such as bullion or rich precipitate.

Outside of smelting and refining, the present-day metallurgy of gold and silver may be summarized under three heads: mechanical methods (concentration, flotation, and blanketing, etc.), amalgamation, and the cyanide process. Chlorination of gold and hyposulphite leaching of silver ores were practically superseded by cyaniding by the year 1900; chloride volatilization and other promising processes have not yet assumed commercial importance. The products of concentration and flotation may be either smelted with lead or copper ore, or may themselves be treated by amalgamation or cyanidation. Each of the latter processes consists of five essential steps.

**Amalgamation:**

Comminution of ore.

Bringing ore in contact with mercury (and with chemicals in the case of silver minerals).

Separating amalgam.

Retorting amalgam to remove and recover mercury.

Melting and refining the crude bullion from the retort.

**Cyanidation:**

Comminution of ore (often combined with auxiliary processes of amalgamation, concentration, or classification, neutralization, or washing out soluble salts).

Dissolving gold and silver.

Separation of solution from ore, and washing residue.

Precipitating gold and silver from solution.

Refining precipitate and melting bullion.

The treatment of placer deposits is a special case of concentration, often combined with amalgamation.

PERCENTAGES PRODUCED BY DIFFERENT PROCESSES IN THE UNITED STATES

(*Mineral Resources, U. S. Geol. Survey, 1921*)

	Gold					Silver				
	1917	1918	1919	1920	1921	1917	1918	1919	1920	1921
Placers; mainly dredging.	25.8	23.6	25.6	25.3	28.9	0.2	0.13	0.15	0.13	0.18
Amalgamation.....	20.9	20.7	31.5	28.5	32.6	0.4	0.3	0.5	0.4	0.45
Cyanidation.....	29.7 <sup>a</sup>	32.2 <sup>a</sup>	28.5	24.3	23.9	16.3	14.3	13.8	13.4	15.7
Smelting ore and concentrate.....	23.6	23.5	14.4	21.9	14.6	83.1	85.3	85.55	86.07	83.67

<sup>a</sup> Including 0.2 per cent by chlorination for 1917 and 1918.

In South Africa about 65 per cent of the recovery is by amalgamation, 35 per cent by cyanidation; on the Mysore Field, India, nearly 90 per cent by amalgamation

## PERCENTAGES BY WEIGHT FROM VARIOUS SOURCES IN THE UNITED STATES

	Placers	Dry or sili- ceous ores	Cop- per ores	Lead ores	Zinc ores	Copper- lead and copper- zinc ore	Lead- zinc ores	Total ounces
<b>Gold:</b>								
1906.....	28.24	63.17	5.77	1.29	0.02	1.26	0.25	4,703,000
1907.....	28.22	62.11	6.44	2.56	0.14	0.05	0.48	4,227,500
1914.....	25.30	66.56	6.00	1.69	0.04	0.01	0.40	4,418,000
1915.....	22.66	67.57	7.22	1.78	0.10	0.05	0.62	4,754,500
1920.....	25.3	63.93	7.18	1.96	0.15	0.16	1.32	2,383,000
1921.....	28.89	66.02	2.25	2.64	0.003	0.007	0.19	2,345,000
<b>Silver:</b>								
1906.....	0.30	29.27	27.69	26.72	0.17	11.88	3.97	57,362,450
1907.....	0.24	36.27	26.58	32.99	0.18	0.93	2.81	52,497,060
1914.....	0.22	39.95	21.30	27.72	0.21	0.36	10.24	69,623,200
1915.....	0.21	35.53	25.96	27.40	1.57	0.33	9.00	72,353,700
1920.....	0.13	36.22	21.49	30.19	2.23	1.18	8.56	56,536,900
1921.....	0.18	51.88	10.36	32.30	0.01	0.97	4.30	46,171,300

## WORLD PRODUCTION OF GOLD AND SILVER, 1923

(Rept. Director of Mint)

	Gold, ounces	Silver, ounces
United States.....	2,426,495	73,295,810
Canada.....	1,223,601	17,754,706
Mexico.....	781,663	90,859,083
North America.....	4,431,759	181,909,599
South and Central America.....	829,892	29,855,073
Europe.....	336,353	8,214,385
Asia.....	1,120,802	10,027,283
Africa.....	10,155,025	1,544,233
Australia and New Zealand.....	876,934	10,867,837
Total for world.....	17,750,765	242,418,410
Total production in ounces from 1492 to 1923, inclusive, based on Soetbeer's figures.....	925,000,000	13,214,000,000

The commercial ratio between the values per ounce of gold and silver was about 15 to 16 from 1800 to 1873; since 1873, the annual average has ranged from 18 to nearly 40. One of the largest producers turns out about a ton of silver per day; one of the largest gold mines has for years yielded a ton of fine gold per month; the value of each output is now about the same.



In hydraulic work the coarse gravel running down the sluices does much of the work of disintegration, and the coarser portion is removed when desired by means of "under-currents" or grizzlies of steep grade, which allow the finer material to pass through and conduct it to boxes or tables where conditions are more favorable for settling. After passing over the grizzly, the coarse gravel may be discarded or returned to the main stream.

A revolving trommel with lifters, and furnished with ample water sprays, is an ideal device for performing these operations on a large scale, and is now standard practice for dredges, the pebbles acting as disintegrators. By graduating the diameters of the holes to suit the material handled, a comparatively uniform discharge may be obtained throughout the length of a trommel, but by far the largest part of the gold passes the holes near the inlet end. Shaking screens have been used but consume too much power. One of the older "cement mills" for hard gravel was virtually a large trommel built of railroad or T-iron. Another cement gravel mill is a pan with a stout vertical shaft carrying agitating arms, and fed with water, accumulated coarse rock being discharged at intervals by opening a door in the side or bottom.

In small operations, the same results are achieved by using a rocker with punched screen, fed a few pounds at a time; or by shoveling into a sluice box, at the head of which is a screen or set of bars, over which the material may be manipulated by a sluice fork or shovel.

The length of wooden sluice boxes is standardized at 12 ft., and a grade of 6 in. means 6 in. per box, or about 4 per cent, the width varying with the load. For small, semiportable boxes, the upper end of the bottom is sawed 2 or 3 in. wider than the lower end, so that they fit closely one in the other.

In large hydraulic work, boulders of several tons weight may enter the sluices and must either be carried through, blasted, or lifted out; such sluices require stout linings of wood or steel.

Various types of riffle material have been used: cross-grain pine blocks, roughly squared, or flat-lying blocks up to 4 by 6 in., either form being separated by small strips of wood or bits of rock; boulders or roughly squared rocks; peeled pine poles;

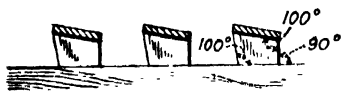


FIG. 1.—Hungarian riffles.

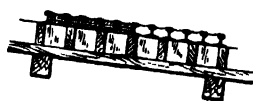


FIG. 2.—Bouery steel-rail riffle at La Grange

planks mortised or bored, or iron blocks cast with channels or pockets, and railroad steel.

Hungarian riffles are strips of wood from about 1 to 1.5 in. square up to 2 by 4 in. laid crosswise with about equal spacing; they are often undercut on the down stream side, and have tops sloping upwards. When subject to heavy wear they are covered with strips of iron or steel, manganese steel being most durable. By attaching them to longitudinal strips they form frames readily removed. A similar riffle for dredges is built of  $1\frac{1}{4}$  or  $1\frac{1}{2}$  in. angle steel riveted to 6 ft. strips of the same material; the angles are opened about 10 or 15 deg. above a right angle, and point down stream. Another effective sluice lining is coconut matting covered with expanded metal (steel lath).

A special study of riffles for heavy work was made by P. Bouery at La Grange, who successfully used 40-lb. steel rails on 5-in. centers, resting on 2 by 6 in. pine strips set edgewise with spacers. He recommends invariably placing riffles crosswise. A riffle of manganese steel designed by Bouery for severe hydraulic work consists of riffle proper, spacers, and lockers; when worn, these can be used as liners.

In cleaning up a sluice, clear water is run for some time, then, beginning at the head, the riffles are removed section by section, the dirt washed off, and the deposited gold washed down to the next section, where it can be scooped up into buckets. It is then taken to a point where it can be panned or treated in a rocker or special sluice to concentrate the gold further, and separate it from the accompanying black sand.

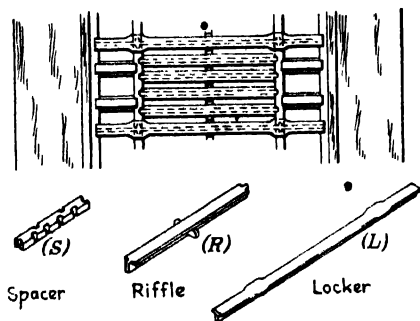


FIG. 3.—Bouery patent manganese steel riffle.

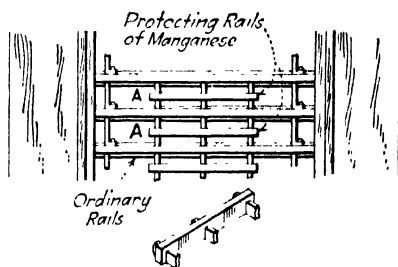


FIG. 4. Railroad rail riffle with manganese protecting rails, at La Grange.

DISTRIBUTION OF GOLD IN SELECTED SLUICES AT LA GRANGE (*P. Bouery*)  
(Boxes 1 to 4 were filled with pebbles, etc.)

Box number	Ounces of gold						Total ounces per 12-ft. box
	+10 mesh	+50 mesh	+100 mesh	+150 mesh	+200 mesh	—200 mesh	
5	45.8	50.7	1.38	0.36	0.31	1.45	100
6-16	18.0	83.3	2.33	1.00	0.31	0.83	43-108
22	1.73	20.22	3.08	0.70	0.25	0.62	26.2
48	0.18	2.18	1.06	0.12	0.05	0.16	4.15
88	0.018	0.12	0.47	0.008	0.026	0.005	0.65
136	0	0.053	0.027	0.043	0.011	0.01	0.14

**Dredges.** The dredges now in general use have close-connected buckets of 5- to 15-cu. ft. capacity, and are built of steel or wood, digging to a depth of 80 ft. below the surface of the pond or stream in which they float.

The buckets discharge into a long, revolving screen or trommel running at a grade of from 5 to 10 per cent toward the stern, where the coarse material passes to the stacker, while the finer portion goes to the gold-saving sluices and may then be run out directly or may go to a second stacker. The land is usually left in a valueless condition, but resoiling is possible by the use of multiple stackers.

The screen may be cylindrical or stepped in diameter, it should have a baffle at the end of each section and must be well braced. In a large dredge it may be 10 ft. in diameter by 50 ft. or more, with a peripheral speed of 150 ft. per minute. The perforations should be adapted to the material handled; one example has openings  $\frac{3}{8}$  in. at the upper end increasing to  $\frac{3}{4}$  in. at the discharge; another  $\frac{1}{4}$  in. increasing to  $1\frac{1}{4}$  in. The stacker belt may be up to 4 ft. wide, of eight-ply rubber, and will normally last a year or more. An internal spray pipe runs the full length of the screen;

and two or more smaller ones outside; these must have an ample supply of water to wash the gravel and carry the fines over the sluices.

The sluices may be in one series or in two decks 4 or 5 ft. apart. They are usually about 30 in. wide, running crosswise of the deck at a slope of  $1\frac{1}{4}$  to  $1\frac{1}{2}$  in. per foot (10 or 12 per cent), and then turning aft. Much the largest portion of the gold is caught in the first few feet of sluices; Janin mentions a 6-ft. dredge with 1,457 sq. ft. of sluice area, catching 89 per cent of the total recovery in 292 sq. ft., or one-fifth of the total area. For more clayey material the area was increased to 3,900 sq. ft. One 15-ft. dredge had 8,000 sq. ft. of sluices in two decks; in another case 4,500 sq. ft. in two decks was found needlessly large for a 15-ft. dredge digging 600 cu. yd. per hour. The head tables are usually kept covered with heavy screen to prevent theft.

A considerable saving is made on the save-all, a small sluice catching the drip from the descending buckets, and discharging through the hull, and in the nugget catcher—a short, steep series of riffles over which the “fines” from the extreme end of the screen pass.

In some cases, as on the Yukon, no mercury is used, and the first section of each sluice is covered with coconut matting and expanded metal. The matting is taken up daily, folded, and washed, and the washings are passed over a special set of riffles. The product is cleaned by panning and finally by dry blowing, while the tailing goes back to the main riffle system. The riffles in the lower sections of the sluices are cleaned up at intervals of a week or two.

In California, mercury is more generally used, up to 3,000 lb. weekly on the larger dredges and up to 1,000 on the smaller. The loss of mercury in a 6-month campaign may range between 1 and 5 per cent of the total used. When cleaning up at intervals of a week or two the riffles are lifted out, section by section, and washed off with a hose, and the dirt concentrated by temporary stops placed in the sluices. The concentrate thus obtained is shoveled out and washed in a small sluice box, the product screened, and the fines run through an amalgam barrel with a little additional mercury.

Sometimes a trough is inserted below a stop to divert the material being washed down into a clean-up box, about 2 by 3 by 1 ft. deep, having several centerboard mercury riffles, the tailing from which passes through a sluice with expanded metal riffles and back to the main dredge sluices.

In many localities, considerable quantities of lead shot, nails, and miscellaneous metallic scrap may be separated in screening the product, and this material may retain more or less amalgam and necessitate working over.

The “black sand” obtained as a by-product in cleaning up placer sluices often contains platinum metals in small proportions, as well as some gold; much of the gold and platinum may be recovered by treatment with a suitable concentrator. The Senn machine has been found well adapted for this purpose.

**Dry Concentration.**—A clean-up of placer material is often finished dry. After removing the coarsest portion with a sieve, the remainder is “tossed” or jigged dry in a pan or shovel, using a circular motion; the sand thus brought to the surface is then blown off. The tailing thus obtained often contains fine or flaky gold.

Dry washers or concentrators are used under desert conditions. The success of all these devices depends on the material being perfectly disintegrated and thoroughly dry; clay, especially, must be pulverized. Several different principles have been applied:

1. Winnowing, by letting material fall vertically through a horizontal blast of air, which is either constant or rapidly pulsating. The wind is often utilized, and the gold caught on a sheet of canvas, but some efficient machines, as that of Edison, have been devised on this principle.

2. Passing the material over an inclined table covered with cloth, supported by wire screen through which a pulsating blast of air rises; the table may be fixed or oscillating, and is provided with low riffles.

3. Passing material over a reciprocating table of the Wilfley type, having a tight cover near the surface, a blast or numerous parallel blasts of air passing parallel to the surface under the cover.

4. Sized material is allowed to fall on a horizontal, rapidly rotating disc (as in the Pape-Henneberg system), the particles being thrown to distances varying with their specific gravity.

**Black Sand.**—The treatment of the black sand or concentrate obtained from beach or alluvial deposits is usually crude and unsatisfactory. This material actually varies much in color; it often consists largely of magnetite and ilmenite, with other heavy minerals such as garnet, tinstone, columbite, or tantalite, and occasionally metals of the platinum group. The gold is retained by, but rarely contained in, the sand particles. The black sand separated by "blowing" at the final stages of a clean-up may show gold values up to \$1 per pound.

Magnetic concentration is rarely of use, as much of the fine precious metal may be picked up mechanically with the magnetic concentrate, while in some cases only a small percentage is strongly magnetic. In some clean river gravels, and such beach sands as the Nome deposit, preliminary separation by 30- or 40-mesh, or finer screens, allows all the gold to pass and retains only pebbles of extremely low grade.

There is no apparent reason why black sand thus concentrated, or recovered from sluices, etc., should not be successfully treated by cyanide solution, after removing coarse gold by riffles or amalgamation. Early experiments are said to have failed in precipitation by zinc, but laboratory tests show no cause for difficulty.

**Blanket Concentration.**—Woolen blankets have long been used for catching gold at Brazilian mines, where mercury is sickened by bismuth and tellurium minerals, and they were introduced into early Californian and Australian mills, and have been used in mills treating the richer Cripple Creek ore. They are generally laid overlapping on inclined tables, the pulp flowing over them for an hour or several hours, when they are folded, replaced by fresh blankets, and the accumulation washed off in a tank.

In 1918, corduroy was used to replace copper plates in the Van Ryn (Rand) stamp mill after adoption of coarse crushing (but not in the tube-mill section), the concentrate (0.27 lb. per ton milled, containing 2.1 per cent gold) was ground in a barrel with mercury, then passing to a mechanical batca. The loss of mercury in the barrel was only 0.01 oz. per ton milled.

In 1923, F. Wartenweiler announced the total elimination of plate amalgamation in two Rand mills, Modderfontein East using five overlapping rows of corduroy strips, which caught, respectively, 80, 11, 4, 3, and 2 per cent of the total catch. The area of corduroy was 1.26 sq. ft. per ton milled daily, and this might have been reduced nearly 50 per cent without serious detriment. The product (1.8 lb. per ton milled) was saved by hand washing, but washing machines might be used; it was treated on a Wilfley, and this concentrate amalgamated in a barrel, yielding 94 per cent of its gold content, 98 per cent of which was free. Corduroy and wool blankets were found equally effective, but corduroy gives a less bulky concentrate, and the lock-up of gold is very small. Canvas gave a still smaller bulk, but caught only 75 per cent as much gold; riffles were only 57 per cent as effective.<sup>1</sup>

<sup>1</sup> The use of blankets, cloth and riffles for gold and other minerals is described in *Agriicola's Book VIII*, see especially pp. 309, 317, 328, and 331 of Hoover's translation. Practice at Grass Valley, Cal., is described by J. A. Phillips "Mining and Metallurgy of Gold and Silver."

them and with some of the one-stamp mills, of which the Nissen is probably the best. This has been made of 2,000-lb. falling weight, with a circular mortar half surrounded by screen. Some others have screen on three of the four sides.

Steel-wire screen is now much used, with either square or rectangular openings, often slot-like, with double wires in one direction and heavily crimped. In fine crushing sheet steel is often used, punched with diagonal slots  $\frac{1}{2}$  inch long, or thin tinned iron plate with round punched holes. The modern screens are almost always set vertical.

In place of a long, line-shaft drive, one electric motor now usually drives ten light or five heavy stamps, by a built-up wood pulley 7 or 8 ft. in diameter with a 14- to 18-in. belt, the shaft running in plain, cast-iron bearings without cover. Wrought-iron cam shafts are preferable to any steel ordinarily obtainable. The cams are preferably attached by the Blanton self-locking device, which allows of easy removal, all the cams being interchangeable in position.

The standard cam curve is the involute of a circle, the center coincident with the cam-shaft axis and the radius the distance from the axis to the central plane of the stamp stems. The involute gives uniform speed of lift, but strikes the tappet with a sudden jar, and the curve is often much modified at root and tip. The gib tappet may have two or three keys. The usual order of drop is 1, 3, 5, 2, 4 (identical with 1, 4, 2, 5, 3), the only combination possible if no adjacent stamps drop consecutively, but 1, 5, 2, 4, 3 (= 1, 4, 2, 3, 5) is also used, and occasionally others in which one adjacent pair drop consecutively. Any tendency to bank sand at one end of mortar is usually overcome by giving the end stamp a slight increase in drop. Various forms of guide are used but generally have cast-iron liners in place of the wood formerly used.

For stamps from 800- to 1,500-lb. weight the following table gives the range of weights commonly adopted. The last column shows the greater range of weight used for heavy stamps in South Africa and India. The percentages are based on falling weight with new shoes.

	800 to 1,500 lb., per cent	1,250 to 2,000 lb., per cent
Stem . . . . .	42-44	47-28
Tappet . . . . .	16-13	10-14
Boss . . . . .	26-28	22-40
Shoe . . . . .	17 14	20-13

The corresponding cam weight ranges from 25 per cent with light, to 20 per cent with heavy stamps, all being about 32 in. across tips. The cam shaft (for 10) 30 per cent above the falling weight for light up to 50 per cent above for heavy stamps ( $5\frac{3}{4}$  to  $6\frac{1}{8}$  in. by 14 to 16 ft.); stems increasing from 3 in. at 800 lb. to 4 in. at 900, and usually 14 ft. long; shoe diameters 8.5 in. up to about 900 lb. and 9 in. above that.

Mortars are always of the high form, of heavy cast iron, generally with front entirely open, but variously proportioned. Reinforced concrete is now in general use for mortar supports, with an intermediate cushion of wood and rubber or belting. The ends and back of mortars are often protected by liners of chrome or manganese steel.

Battery water should be supplied at the rear of the mortar at two or more inlets; the ratio of water to ore stamped has varied widely, ranging from 2.5 in occasional Californian mills to 10 or 12 in former Homestake practice, high crushing duty and amalgamation being obtainable at both extremes—5 to 8 is generally preferable.

With plate amalgamation, the water and grade must be sufficient, and the distribution of pulp over the topmost plate even enough to produce uniform waves and avoid building up islands of sand. For successful amalgamation the temperature of the feedwater should be uniform, and neither extremely cold nor hot. Practically all the energy expended in crushing reappears in the increased temperature of the pulp, which is of importance in cold climates.

**Amalgamation.**—Mortars formerly had inside plates both front and back 6 or 8 in. wide and extending across the full length; the back plate has been discarded and the front plate—usually about 5 or 6 in. by  $\frac{1}{4}$  in. thick—is attached to the chuck block immediately beneath the screen; even this is now obsolescent, and is seldom used with heavy stamps.

A "lip plate" is sometimes attached outside the mortar, extending across the discharge and 1 to 2 ft. wide. The main apron plate may be in one unit or more, each 4 to 5 ft. wide by 8 to 12 ft., of  $\frac{1}{8}$ -in. soft-rolled copper. In successive units, the width should be maintained or increased. Long plates are usually set in an unbroken sheet of 8 to 24 ft., but some operators claim an advantage in cutting them into 2-ft. lengths, set with a drop of an inch or two at each step; the long plates are easier to clean and care for. Plates of Muntz metal have been used in New Zealand and elsewhere with apparent success; at several mills in the United States they have been a total failure. The plate table is best built of tongue-and-grooved lumber, 1.5 or 2 in. thick, with 2-in. sides; and may be made adjustable in slope. Planed cast iron has been used. The plates are secured by screws or copper nails, and cleats are often added at the sides. If divided longitudinally into two or three runs it is easy to clean one run at a time without stopping the battery.

The inclination of plates is best kept from 1.5 to 2.5 in. per foot (12.5 to 20 per cent) depending on the proportion of water, fineness of pulp, and proportion of heavy minerals, but extremes of  $\frac{5}{8}$  in. up to 3 in. per foot have been used. The plates are usually placed close to the mortar, but sometimes the pulp is transported some distance and then redistributed over a plate system. This sometimes results in large accumulations of amalgam in pipes or launders.

Silver plating of the copper plates is advantageous, except with rich ore, and in the case of the plate next the mortar; about 2 oz. silver per square foot is a suitable amount, or soft silver amalgam may be rubbed upon the plate. In "setting" new copper plates, about  $\frac{1}{4}$  oz. mercury per square foot is requisite, and this should be applied by scouring with wet sand, and a little weak solution of sodium cyanide.

Various amalgam or quicksilver traps have been used, but there is probably nothing better than a shallow, transverse trough or riffle about 2 in. deep and 4 or 5 in. wide at the foot of the plate table. The accumulated concentrate from this may be collected daily with a small scoop and carried in buckets to a central point, where it can be run over a special plate or riffles, or ground in a pan or small ball mill.

Many mechanical amalgamators have been devised and used, such as horizontal rotating cylinders lined with copper, or provided with copper wings or lifters, or arrangements of horizontal discs or shelves rotating on a vertical axis, series of shelves of sheet copper, etc. The Pierce amalgamator is probably the only one of these to show greater efficiency than a plain plate. Numerous electrolytic devices have also been used, as well as sodium and zinc amalgam, to maintain the surface of mercury in a bright condition.

It is remarkable that gold or amalgam, while escaping all the contrivances arranged to catch it, often accumulates in unexpected places, such as angles of cones, sumps, and launders, the rakes of Dorr classifiers, and on the runners of high-speed centrifugal pumps. All such places should be inspected from time to time, and any tendency to build in launders should be encouraged by placing riffles suitably safeguarded.

**Plate Area.**—The relation of plate surface to stamps and stamp capacity varies remarkably in the practice of different fields. Some extreme cases may be noted:

Mine or district	Approximate percentage of product amalgamated	Square feet plate area	
		Per stamp	Per ton per day
Treadwell, Alaska—880 stamps, 1904.....	50	9	2
Homestake, Amicus mill, 240 { 1910.....	70	62 1	13.6
S. D. stamps { 1923 with tubes.	66	43.3	7 8
Pocahontas mill, { 1910 . . . . .	70	32.7	7.5
160 stamps { 1923.. . . .	66	18 0	3.6
South mill, 120 { 1923 with rod } mills	66	25.6	1.6
Rand, South Africa—Typical mill with tube mills	65	10	1 2
Ooregum, India—55 stamps, 1923 with tubes...	88	20	2 2

With the revival of blanket practice the tendency is to reduce plate area still further.

**Loss of Mercury.**—In gold amalgamation, an ounce per ton was not an uncommon loss in early practice, and occasionally much higher losses were recorded, but this has been much reduced. At the Treadwell mines, shortly before abandoning amalgamation, the loss varied from 0.06 to 0.08 oz. per ton with ore from \$1.50 to \$2.50; at the Homestake, 0.06 oz. was lost with low-grade oxidized ore, and 0.17 oz. with \$5-ore containing sulphides, and a similar range has prevailed in South Africa. At Modderfontein East, amalgamating corduroy concentrate, about 0.05 oz. is reported.

Among the principal sources of loss are drops running from the end of plates kept too "wet," and flouring.

Outside plates usually have the amalgam removed once every 24 or 48 hr. by washing off sand and then brushing thoroughly after sprinkling with some additional mercury. The amalgam may then be collected at one spot by means of a stiff brush or cloth, or a rubber scraper, and transferred to an iron kettle. Any hard, crystalline accumulations should be carefully scraped off before they become persistent. With a properly organized system the entire time consumed is about 1 min. per stamp per day. In many mills the plates are also "dressed" or brushed up at intermediate periods, and may be sprinkled with mercury at the same time. Inside plates are usually removed for cleaning about twice a month, a clean plate being exchanged for the one taken out. The entire mortar is cleaned out about once a month, or whenever dies are taken out.

The actual absorption of precious metal into the body of a copper plate is negligible, but the accumulation upon the surface may amount to many dollars per square foot if accretions of hard amalgam are allowed to build up, as they sometimes do, to a thickness of  $\frac{1}{8}$  in. or more, thus tying up an important amount of gold. In some mills this layer is softened by the occasional application of steam or hot sand, which facilitates its removal by scraping, but it is better to avoid this condition by daily removing hard accretions. Absorption only occurs when the rolled copper plate has capillary openings, such as minute cracks or pinholes.

Amalgam obtained from plates, etc., is cleaned by grinding with water and additional quicksilver, the floating impurities being wiped from the surface with a sponge, or in small lots by pouring from one vessel to another, when pyrite, etc., adheres to the moist vessels. Metallic iron is removed by a magnet. Small lots are ground by hand with a pestle and mortar of iron or wedgewood ware; on a larger scale the amalgam, or accumulated cleaning, is treated in a miniature iron tube mill, or a Knox or Berdan pan. The tube mill may be 2 ft. in diameter by 1 to 4 ft. long, with steel balls or rods of drill steel; it may be worked in batches through a covered hand hole, or continuously by a stream of water passing through hollow trunnions. The Knox pan is a small cast-iron pan with a muller carried on a vertical shaft; the Berdan revolves on an inclined shaft, grinding by means of two or three large balls, or by drugs chained to a fixed post.

The amalgam is squeezed in fairly heavy (10-oz.) canvas; the finish is usually given by hand in balls of about 100 oz. each, or in cylinders compressed in a hydraulic machine with discs of canvas and coconut matting at each end; the removal of excess mercury is facilitated by heating the balls in hot water.

A high "percentage of retort" is favored by: a large percentage of gold in the resulting bullion; coarseness of the original particles of native gold; frequency of clean-ups (giving mercury less time to penetrate); pressure applied in squeezing (much increased by use of machine); and high temperature during the squeezing. About 60 per cent is occasionally reached, while silvery amalgam may yield only 25 per cent; 35 per cent is about an average for hand-squeezed amalgam.

Amalgam retorts are made in the pot form for charges up to about 2,000 oz., and should be not over two-thirds filled. For larger amounts the cylindrical built-in form should be used, fitted with three or four light, cast-iron trays. The trays or pot retorts are given an internal wash of wood ashes, fine clay, or chalk, or are painted with iron oxide, to prevent adhesion of bullion. Paper is sometimes used, but may cause flouing of the mercury. The covers or doors are best sealed with a lute made of sifted wood ashes, and secured by well-driven wedge keys. A long condenser should be used, with a jacket supplied with cold water. In large retorts it is convenient to use loose dividing pieces of sheet iron, similarly painted, so that the resulting bullion will readily fall into pieces of convenient size for charging into crucibles.

Any convenient fuel may be used in retorting, and a pot retort may be heated in any style of melting furnace, or in the open if surrounded by a piece of sheet iron, but it is essential that the top be covered and kept hot, or the mercury vapor will condense before escaping. The temperature of boiling mercury is 356°C. (672°F.) and its latent heat 125 B.t.u. per pound. On account of the high specific gravity of the vapor (seven times that of air), the discharge pipes should point downward as far as possible and means should be adopted to carry off any escaping fume and prevent its inhalation, especially if it is necessary to open the retort before it has time to cool. The mercury carries over a trifling amount of gold, most of which is due to spattering in the earlier stages of volatilization. The loss of mercury should be very small; any considerable difference in the weight of amalgam and of bullion plus mercury points to a defective lute or a leaky retort.

Bars of mill bullion or refined cyanide product are melted in graphite crucibles with borax sufficient to form a cover, and poured into iron molds previously smoked heavily or coated with graphite. About 2,000 oz. is the usual weight limit for gold bars, and about 1,000 to 1,200 oz. for silver.

Bars containing gold and silver with little base metal other than copper, suffer very little segregation and solidify rapidly. In sampling them it is safe to chip from one corner at the top and the opposite corner at the bottom or to drill  $\frac{1}{4}$  in. or  $\frac{3}{8}$  in. holes at opposite corners. Cyanide bars containing lead or zinc are irregular in compo-



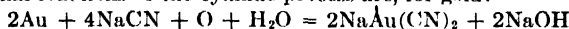
sition, and should be sampled from the crucible just after stirring, or a sample may be taken while pouring by deflecting some of the flowing metal into a vessel of water.<sup>1</sup>

As soon as the bullion solidifies in the mold, the slag may be removed by pouring water on it and scraping it out, or by plunging the hot bar into cold water. Plunged bars retain a little water if the surface is rough.

### CYANIDATION

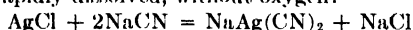
**Cyanidation.**—At the present time sodium cyanide (NaCN) has entirely superseded potassium cyanide (KCN) as a solvent, and it alone will be considered here, although some metallurgists still make all calculations in KCN and recalculate the results to the actual salt used.<sup>2</sup>

The essential reactions of the cyanide process are, for gold:



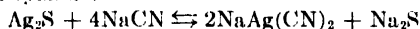
This is Elsner's reaction, verified by MacLaurin, indicating the necessity for oxygen or its equivalent. Metallic silver follows the same reaction, substituting Ag for Au. Cyanides of other alkali and alkali-earth metals act in precisely the same way, substituting Ca, Ba, 2K, etc., for 2Na. Hydrocyanic acid is an extremely feeble solvent, and cyanogen itself is without action on gold.

Silver chloride is rapidly dissolved, without oxygen:

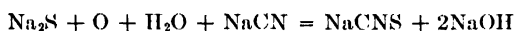


and most other silver compounds are similarly dissolved.

Silver sulphide, however, dissolves slowly, the reaction being reversible and requiring an excess of cyanide:



Artificial gold sulphide is similarly dissolved. The solutions obtained always contain more or less thiocyanate (NaCNS), and this probably results from oxidation of the  $\text{Na}_2\text{S}$ .



Free sulphur, resulting from partial oxidation of pyritic ore, or sulphur from thiosulphates formed by the action of lime or soda on pyritic ore, also reacts on cyanide with formation of thiocyanate:



Tellurides of gold and silver are scarcely affected by cyanide solutions, and silver selenide is very slowly attacked.

ELECTROMOTIVE FORCE OF METALS IN CYANIDE SOLUTIONS<sup>2</sup>

Concentration  KCN	Most probable value for e.m.f.						
	Zinc	Copper	Gold	Silver	Lead	Mercury	Iron
6.5 per cent = $N$ . . . . .	+0.945	+0.930	+0.42	+0.34	+0.20	+0.15	-0.03
0.65 per cent = $N/10$ . . . . .	+0.870	+0.68	+0.265	+0.195	+0.16	+0.05	-0.09
0.065 per cent = $N/100$ . . . . .	+0.775	+0.43	+0.09	+0.055	+0.11	+0.04	-0.12
0.0065 per cent = $N/1000$ . . . . .	+0.415	-0.05	-0.34	-0.31	+0.07	-0.19	-0.13
0.00065 per cent = $N/10,000$ . . . . .	+0.385	-0.25	-0.45	-0.42	+0.05	-0.59	-0.14

<sup>1</sup> See p. 110, "Sampling," this book

<sup>2</sup> It is convenient to remember that, for all practical purposes: 4 lb. KCN = 3 lb. NaCN, and 1 lb. of 98 per cent NaCN = 2 lb. of "Aero" containing cyanogen equivalent to 49 per cent NaCN. Also that 10 c.c. of  $N/20 \text{ AgNO}_3$  (8.50 g. per liter) = 0.049 g. NaCN = 0.05 g. of 98 per cent salt, or 0.1 g. of "Aero" at 49 per cent.

<sup>3</sup> CHRISTY, S. B., *Trans. A. I. M. E.*, **30**, 921-922.

As calculated from the chemical equivalents, 1 lb. NaCN suffices to dissolve 1.1 lb. Ag or 2 lb. Au; 1 lb. Zn to precipitate 3.3 lb. Ag or 6 lb. Au. An ounce of metallic silver, therefore, requires 1.8 times as much of either reagent as an ounce of gold, and a dollar's worth of silver at the ordinary range of price uses forty to sixty times as much as a dollar's worth of gold. In practice, the difference is even greater because, as a rule, gold dissolves readily in dilute solution, while silver often occurs as the sulphide which requires a stronger cyanide solution owing to the reversible character of its reaction. On the other hand, silver chloride dissolves rapidly and with little decomposition of cyanide.

Under identical conditions, metallic silver dissolves about half as fast as gold, or in exact proportion to their atomic weights. Silver-free gold dissolves more readily than gold alloyed with silver. Maclaurin showed that all gold-silver alloys should dissolve in cyanide solution at the same rate as measured in thickness removed, and in the same proportions in which they exist in the original alloy; Yokobori and others confirm this.

As regards the effect of amalgamation on the rate of dissolution by cyanide, some contrary evidence has been adduced. In stationary beaker tests with pure gold foil a mere film of amalgam retards solution about as much as thorough wetting with mercury—similar pieces show one-half to one-tenth the rate of solution noted with clean gold; when agitated in sand mixtures the same tendency is noted.

For a given percentage of NaCN, gold in a thick slime mixture dissolves much less rapidly than in thin pulp, the same is true of silver, of oxygen, and of salts such as NaCN itself—lumps of which should not be dumped in agitators but predissolved in clear solution or water. This effect seems to be partly due to the greater viscosity of thick pulp, partly to the smaller proportion of solution to unit volume and unit surface.

After a certain period of contact with a given solution, the dissolution of gold from ore practically ceases, in spite of agitation and ample aeration; on adding fresh solution, or replacing a part with barren solution or even with water, further dissolution takes place. This is more marked with silver than gold, and especially on adding aerated barren solution from extractors. Some of the effect is, no doubt, due to the inert or "fatigued" solution having reached an equilibrium with the ore, but probably much of the later apparent dissolving is actually diffusion of the richer solution adsorbed, or absorbed by the ore particles.

In sulphide ores, especially complex sulphosalts, silver may be very slowly soluble; this may often be partly overcome by removal from the solution of the  $\text{Na}_2\text{S}$  formed by means of lead compounds; mercury salts are sometimes used with advantage, and fine grinding is essential. Owing to the reversible character of the reaction with  $\text{Ag}_2\text{S}$ , a short treatment with very strong (1 per cent or more) solution of NaCN is often much more effective than long treatment with dilute.

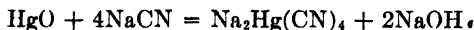
The best strength of solution must be determined by experiment. In agitation systems, coarse gold being removed if originally present, slime may be treated with solution of 0.1 to 0.01 per cent NaCN; silver slime may require 0.2 to 0.5 per cent or higher.

In well-roasted sulphide ore or concentrate the gold is, as a rule, amenable to cyanide, but the globular particles from roasted tellurides dissolve slowly; silver in similar roasted material becomes partly insoluble; extremely fine grinding is desirable with most rich silver material. After fine grinding, such material is sometimes put back in the same circuit with average ore; it is best first to give it a separate intensive treatment with strong solution.

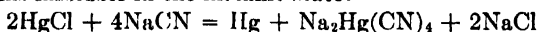
Gold telluride ores must either be roasted or treated with some oxidizing agent, such as bromocyanide ( $\text{BrCN}$ ), after preliminary leaching; or any alkaline bromate, or peroxide of sodium or barium, may be used after preliminary treatment with NaCN.

Many other oxidizing agents have been tried in connection with cyanide treatment, to supply "nascent CN" or its equivalent, but none has been able to compete with atmospheric oxygen for ordinary ores.

**Lead and Mercury in Cyaniding.**—Mercuric oxide and chloride dissolve completely in cyanide solutions



but when mercurous oxide or chloride is treated with alkaline cyanide half the mercury remains insoluble in the metallic state:



An old tailing pile containing HgCl, therefore, cannot be expected to yield 50 per cent of the mercury by cyaniding; mercuric oxide would give an almost complete recovery; the sulphide and metallic mercury would yield little or nothing.

Lead is sometimes added to solutions as the acetate (54.6 per cent Pb) or nitrate (82.56 per cent Pb), the latter being generally more economical. Litharge (PbO = 92.8 per cent Pb) is sometimes added to grinders, or ground with lime. In alkaline solutions the lead is dissolved as plumbite ( $\text{Na}_2\text{PbO}_2$ ), which reacts with sulphides to form PbS. Occasionally, a local oxidized lead ore ( $\text{PbCO}_3$ ) has been similarly used. Removing  $\text{Na}_2\text{S}$ , lead facilitates the solution of  $\text{Ag}_2\text{S}$  (argentite), but it has no beneficial effect on the complex sulphosalt ores of silver. Mercury would similarly precipitate the sulphide radical as  $\text{HgS}$ . Both lead and mercury also influence precipitation. Contact with zinc dust or shaving at once throws down metallic lead or mercury, forming a zinc-lead or zinc-mercury couple which facilitates precipitation of gold and silver, and is especially advantageous when zinc shaving is coated with copper. Lead added to solutions at the time of precipitation is found in the precipitate, and is sometimes troublesome in refining unless cupellation is practiced. Any mercury in solution is similarly precipitated, and when zinc precipitate contains much (say 10 per cent) of it, its removal by distillation may be profitable.

**Losses of Cyanide.**—Losses of cyanide are mechanical and chemical. The first comprise the cyanide that is carried off in solution, some of which may be unavoidably thrown away daily, to prevent accumulation of too great a volume, or may be discharged in the residue, the washing of which is necessarily imperfect.

Chemical losses include that due to hydrolysis of NaCN ( $2\text{NaCN} + \text{H}_2\text{O} = 2\text{NaOH} + 2\text{HCN}$ ), but this effect is slight in solutions which are distinctly alkaline, and is much smaller in old solutions (which often carry most of their CN in the form of  $\text{Na}_2\text{Zn}(\text{CN})_4$ ) than in simple NaCN; decomposition of NaCN by acids, including  $\text{CO}_2$  contained in air used in agitation ( $2\text{NaCN} + \text{CO}_2 + \text{H}_2\text{O} = \text{Na}_2\text{CO}_3 + 2\text{HCN}$ ); oxidation of NaCN by oxygen of air to form NaCNO and other inactive compounds, such as bicarbonates ( $\text{NaCN} + \text{O} = \text{NaCNO}$ ;  $2\text{NaCNO} + 3\text{H}_2\text{O} = \text{Na}_2\text{CO}_3 + 2\text{NH}_3$ , etc.); reaction with iron compounds, copper, etc., to form Prussian blue and various double cyanides, and with sulphur to form NaCNS.

**Cyanicides.**—Cyanicide is a convenient name applied to all those substances found in ores and tailings which cause a loss of the essential ion CN from the solutions used in treatment. Under this head may be grouped acids which directly decompose NaCN (including carbonic and humic acids); salts such as sulphates and arsenates, especially those of iron, which consume free alkali ( $\text{Ca}(\text{OH})_2$  and NaOH) thus facilitating the hydrolysis of NaCN; ferrous salts and oxidized compounds of copper and zinc which form complex cyanides, either entirely inert or feeble solvents for gold and silver; and certain sulphur compounds which react with NaCN to form NaCNS.

When used injudiciously and in excess, even oxygen, chlorine, bromocyanide, peroxides, and other oxidizing agents are actually cyanicides. The cyanide actually used in dissolving gold is almost negligible, but rich silver ore consumes more—100 oz. of silver using over 6 lb. NaCN to form the double cyanide.

Copper in oxidized ores is usually in the form of the green or blue carbonate (malachite or azurite), an oxide, basic sulphate, or occasionally the metal. In pan-amalgamation tailings it occurs in similar forms from decomposition of added sulphate. In all these forms it is readily dissolved by cyanide solutions and decomposes or renders useless approximately three times its weight of NaCN, or four times of KCN. In the case of KCN, the actual cuprous compound formed appears to lie between  $K_2Cu'(CN)_3$  and  $K_2Cu'(CN)_4$ , while a portion of the CN is oxidized to CNO in reducing combined 'u' to Cu'. As little as 0.1 per cent of soluble copper may, therefore, cause a loss of several pounds of cyanide per ton treated. Unoxidized sulphide ores are commonly but little attacked and decompose relatively little cyanide.

From some oxidized ores it is possible to remove the soluble copper by dilute ammonia, or, if but little calcium carbonate is present, by dilute sulphuric acid; in either case the dissolved copper must be removed by thorough washing before contact with cyanide solution.

Iron and steel in the form of sheet metal, etc. are practically without effect on cyanide solutions. Some writers have insisted that the fine, metallic iron introduced into ore by wear of mill castings, steel balls, and rods, etc., which may range from 1 to 5 lb. per ton, decomposes cyanide and interferes with gold extraction. In practical tests, it is difficult to recognize any losses due to metallic iron as such. Any actual decomposition is probably due to ferrous compounds produced by oxidation of this finely divided metal, or by the action on it of acids resulting from oxidation of sulphur compounds in the ore.

**Antimonial Ores.** - Ores containing antimony as sulphide (stibnite) have, in some instances, given trouble in extraction, and also by yielding an impure precipitate, difficult to refine unless cupellation is practiced.

Fine grinding has been recommended, and the use of a solution as low as possible in cyanide and especially low in free alkali. In other cases some success has been reported in the adoption of a treatment with comparatively strong solution of sodium hydroxide or sulphide to dissolve interfering antimony compounds, and washing out the solution before cyaniding.

In some antimonial ores, as with others containing Se or Te, all or most of the gold may resist both amalgamation and cyanide, and may also be impossible to concentrate. A thorough roast, followed by fine grinding, generally renders a high percentage soluble in cyanide solution.

**Arsenical Ores.**—Many of the common arsenical minerals, notably arsenopyrite ( $FeAsS$ ), are totally unaffected by cyanide solution; their oxidation products are, however, soluble in many cases. When arsenic passes into solution, some of it may appear in the precipitate, and in this case extreme precautions must be taken in disposing of the fumes from acid treatment, which may contain arsine ( $AsH_3$ ).

The presence of manganese minerals in gold ores appears to have no ill effect in cyaniding; some silver ores contain large percentages of manganese peroxide but yield readily to cyanidation; others, some of them containing relatively small proportions of manganese, yield only a few per cents of their silver, even to strong cyanide solutions. Mere addition of  $MnO_2$  has no prejudicial effect, and it is probable that in the latter ores a more or less definite manganite of silver exists, analogous to the com-

pounds of barium and copper found in psilomelane. Investigations by R. Linton, E. M. Hamilton, and W. H. Coghill show that in some cases treatment with dilute hydrochloric acid, salt and sulphuric acid, sulphur dioxide, hydrogen sulphide, or a sulphhydrate, or a chloridizing roast leaves the silver in a form permitting a high extraction with cyanide solution, though it may be insoluble in nitric acid. Reagents which decolorize the dark manganese compounds generally free the silver.

For instance, Hamilton, in one case, extracted only 5 to 15 per cent at 200 mesh, additions of lead, oxidation, hot solutions, chlorine, and sodium sulphide ( $\text{Na}_2\text{S}$ ) giving no improvement. A preliminary treatment with  $\text{H}_2\text{S}$  or  $\text{NaHS}$  increased the extraction to 73 per cent,  $\text{HCl}$  to 94 per cent, 5 per cent  $\text{SO}_2$  to 84 per cent, and a chloridizing roast to 75 per cent, when followed by agitation with dilute  $\text{KCN}$  solution. Concentration, oil concentration, and flotation gave no results.

The Caron process commences with a "reducing roast" to decompose peroxides, and in certain cases has greatly increased the subsequent extraction of silver.

Calcium sulphate is sometimes an original constituent of ores and tailings and of some waters; more commonly it results from the roasting or weathering of calcareous ores containing sulphides, and occasionally from the action of sulphuric acid on such ore. Lead sulphate may also react with limey solution to give a saturated solution of  $\text{CaSO}_4$ . In Colorado and Western Australia leaching of roasted ore has sometimes been followed by the setting of charges to a cement-like mass, which might require blasting. A more common result is the supersaturation of cyanide solutions with  $\text{CaSO}_4$ , which crystallizes as a hard deposit on pipes, canvas, etc., and may coat zinc shavings so as to render them inactive. A complication is caused by the fact that the solubility of  $\text{CaSO}_4$  in water decreases with a rise of temperature.

Magnesium sulphate may be similarly formed; while readily soluble, it is equally objectionable owing to the flocculent precipitate formed when its solution is mixed with another differing in alkalinity.

Owing to the presence of carbonaceous matter (not graphite) in black schists associated with the ores, it has been impossible to secure good extractions of gold at certain mines in various parts of the world, much of the gold being reprecipitated as soon as dissolved in some form which has never been positively identified, though much has been written on the subject. Charcoal from charred mine timbers, etc., similarly interferes.

In the case of some African ores, a process was worked out by Feldtmann and Wartenweiler for extracting the reprecipitated gold by a subsequent leaching with sodium sulphide solution.

A more recent method is that of Silver and Dorfman, who give the ore a preliminary agitation with a little flotation oil, which prevents the carbonaceous matter from interfering.

Some pyritic concentrates oxidize rapidly to  $\text{FeSO}_4$ , etc. and then decompose large amounts of  $\text{NaCN}$ , forming ferrocyanides, Prussian blue, etc. This may be obviated by a fairly long aeration in the presence of lime or soda, oxidizing the iron completely to ferric hydroxide.

At the Goldfield Consolidated mill the concentrates contained copper as well as iron sulphates. Soluble copper and iron were removed by preliminary treatment with dilute sulphuric acid, followed by an alkaline wash, after which the fine-ground concentrate was cyanided in a Pachuca tank with repeated decantation, finishing in a Kelly filter.

**Lime** is used in cyaniding to neutralize acid existing in ore, or the "latent acidity" of such salts as basic ferric sulphate, thus protecting cyanide from decomposition. It is also of value in increasing the settling rate of slime.

When crushing in water quicklime may be fed dry with the ore, or may be slaked or ground in a tube mill or pan. This early introduction effects neutralization at the

earliest possible stage, but sometimes has an adverse influence on amalgamation. It is advisable when crushing in cyanide solution. An opposite policy is followed at the Homestake sand plants, where the ore develops acidity by oxidation and a granular lime is required for progressive neutralization; here it is crushed by a stamp through a 7-mesh screen and mixed with the sand just as it passes to the collecting-leaching vats.

In treating dry sand, the lime should be slaked carefully, and the fine product mixed as uniformly as possible with the charge at any convenient stage. With slime pulp, it may be used as milk of lime fed from a grinding pan or mixer. Acid and bicarbonate waters consume an appreciable quantity of lime. In some cases, as when aluminum is used as a precipitant, the calcium in solution must be replaced by sodium, by the use of caustic soda or soda ash.

An excess of alkali in solution protects NaCN from hydrolysis, but it usually retards and may even prevent the dissolving of gold and silver, especially with sulphide ores. Alkalinity must, therefore, be carefully controlled, and it is generally best to maintain it at the lowest possible point in excess of that corresponding to the cyanide (NaCN) indicated by titration—in other words, the protective alkali should be as near to zero as possible. This is generally safe, as old solutions containing zinc show little tendency to hydrolysis of HCN.

Lime should be free from charcoal and contain but little magnesia. The available CaO in good quicklime is between 80 and 90 per cent; it is easily determined by shaking 2 g. with 20 g. of sugar in 200 to 1,000 c.c. of distilled water, and titrating one-twentieth of the clear liquid with standard acid.

**Sand and Slime.**—In the first MacArthur-Forrest patents, agitation in cyanide solution is indicated, but in the early practical plants some form of separation was found necessary, the coarser material, including as much of the fines as possible, was leached, the "slime" being allowed to accumulate untreated, unless exceptionally rich.

"Slime" properly refers to colloidal material—"superfine particles"—which can neither be leached nor settled readily; Gross has defined it as "anything which renders water muddy." The slime separated by classification is largely extremely fine sand, the microscope showing this to consist of crystalline particles. Leachable sand may contain 40 or 50 per cent of material finer than 200 mesh, provided true (colloidal) slime is practically eliminated. In general, quartz and pyrite tend to pass into sand during classification, while the slime contains the more basic and hydrous constituents of the ore—especially limonite, and hydrous silicates of alumina and magnesia, such as kaolin and chlorite.

In rare instances, a porous ore, containing no coarse gold, may be crushed coarsely (to, say  $\frac{1}{4}$  in.) and leached directly, but classification is more generally necessary.

"All-sliming" is a term loosely applied to the comminution of an ore to pass 200 mesh—sometimes extended to 100, or even 80 mesh—the general idea being to insure a product which can easily be kept in suspension.

Crushing in cyanide solution was first attempted by A. B. Paul in California, but was little used until 1899; since then its use has rapidly increased. Milling in water washes out soluble cyanicides, and lime may be used to neutralize latent acidity, in some cases saving much cyanide; amalgamation may be thus kept in advance of contact with cyanide. Crushing with cyanide complicates the sampling of heads, owing to dissolved values, but has many advantages, dissolution of gold beginning as soon as the ore enters the mortar or mill, and the only water introduced into the system being original moisture and that used as a final wash. From 50 to 75 per cent of the soluble gold may dissolve during milling, but with silver solution is much slower.

**Sand Leaching.**—Sand is leached in vats with filter bottoms, filtration being effected by gravity, in some cases aided by the application of a vacuum beneath the filter. The vats are cylindrical, of steel or wood, redwood or cypress being generally preferred on account of their durability. They must be made absolutely water-tight, with substantial foundations, preferably parallel walls of concrete arranged to allow of easy inspection of the bottom and sides. Vats of reinforced concrete have been used, of various shapes, made tight by the use of bituminous coatings. Wooden vats should have the staves doweled, bottom boards either doweled or grooved for the insertion of pine tongues, and bottom end joints made with metal tongues. The bottoms should have a slight slope toward the solution outlet.

**Filter Bottoms.**—A ring of wood is placed around each bottom, about 1.5 in. from the staves or side, forming an annular channel for the rope used to secure the stretched filter; the height of this varies, but should be 3 to 5 in. for large vats. The space inside this ring is occupied by some form of wooden grid of equal depth. One of the best forms is a system of parallel strips, set edgewise and notched or crozed on the under side for half their depth so as to allow of free circulation. For instance, the strips may be 2 by 4 in. or 2.5 by 5 in. with notches 4 or 5 in. long and 4 or 5 in. apart; the strips themselves are nailed down 2 or 3 in. apart. A similar effect is produced by continuous 2- by 2-in. strips laid parallel and resting on similar but short pieces 6 in. apart, laid crosswise on the bottom with spaces between their ends; or the parallel strips may rest on short blocks through which the nails pass.

Upon the strips is laid a circle of coconut matting, sewn and hemmed, and fastened on the ring by occasional nails or staples. Over this is the filter proper, of heavy canvas, cut somewhat larger than the tank bottom, tightly stretched, and fastened by driving an inch rope into the recess round the tank bottom. In South Africa, hessian (hurlap or hop cloth) has been laid on the wood grid, and coconut matting above this. When vats are discharged by shoveling, the upper cloth must be protected by boards, say 6 in. wide and a few inches apart, or by wider boards with numerous holes 1 in. or larger.

Around bottom discharge doors a tight wood ring is built up, of the same height as the filter. Near solution outlets all approaches must be kept clear. Near such outlets it is well to have a movable false section of bottom, which can be lifted occasionally to remove accumulated fine sand which may pass through holes in the filter. The canvas filter should have a valve or opening, which can be closed by tying a sleeve sewn into it, to release air when the water is introduced.

**Discharge Openings for Sand Residues.**—These may be placed in the bottom of the vats or in the sides close to the filter bottom. In the latter case some of the hoops or rods for wooden vats must pass round the gate frame, or connect with the frame. Sluicing gates in the bottom should be near the sides, with one in the center of a large vat; for shoveling they should be so distributed that each serves a nearly equal area, but they should also be placed in straight lines so grouped as to require a minimum number of car tracks or sewers beneath the vats.

Side doors are rectangular; bottom doors may be round; they open outwards and are conveniently hinged; and secured when closed by swing bolts or by a hinged lever arm tightened by a swing bolt. They may be of pressed steel or cast iron, made tight by square packing. A convenient center gate is that of Merrill, closing tight on

an iron ring, and lifted from above by a threaded central rod in a column of pipe; the latter may also serve as support for a movable Butters distributor. To diminish resistance in lifting, such bottom valves should be made with the top an acute cone.

Leaching vats may be filled with current mill pulp, or with fair sand, conveyed by water or solution, or with dry sand or crushed ore. The main consideration is to secure uniform distribution and uniform permeability. If loaded wet, the vat should be first filled, or at least partly filled, with water or solution.

The total overflow during filling = original water + conveying water - interstitial space in charge = original water + total volume pulp fed - net volume of sand in charge.

Wet sand is usually fed through a Butters-Mein distributor (the revolving lawn-sprinkler type) with six or eight arms of 1½- or 2-in. pipe of differing lengths ending in elbows with flattened lips. For uniform filling the tank bottom is divided into equal annular areas, each radial pipe terminating nearly over the middle of a ring. The overflow is carried off by an annular launder, usually outside the staves, but sometimes built inside. With cheap labor, as in Africa and Mexico, filling was often done by a man with a hose.

As soon as filled, the sand is allowed to drain, and solution is applied to the top; it may be applied as a spray or allowed to pour upon the sand—in the latter case sheet-iron pans are used to prevent washing holes in the surface.

In filling with dry or drained sand, conveyors may be used—a main belt running along or between rows of vats, with a traveling shuttle belt across the vats—with automatic discharge. Or the feed may discharge over the center of the vat, and slide down a radial inclined shoot with adjustable openings, the shoot being gradually moved round the vat by hand. Or barrows, cars, etc. may be simply dumped over a coarse grating supported just above the top of the vat.

When filling with dry or drained sand, some hours of treatment time may be saved by simultaneously introducing solution below the filter bottom, so that it rises through the sand about as fast as the sand accumulates. As soon as the vat is filled and solution reaches the top, the bottom supply is cut off and normal downward leaching is started.

Direct treatment in the same vats in which sand is settled wet is only practicable when colloids are absent or have been washed out almost completely by cones, *spitzkasten*, or other classification systems. Filter-bottomed collecting vats are sometimes used, and may be superimposed above the treatment vats, the settled sand being transferred to the latter by shoveling or by an excavating machine, such as the Blaisdell. Instead of an annular overflow launder for the collecting tank, vertical slots have been used in Africa for overflow water outlets, the outflow level being automatically raised by roller-blind devices carried on floats, or it may be raised by cast-iron rings placed above a bottom opening.

In double treatment, the sand is collected and drained in such tanks, and given a preliminary cyanide solution treatment to displace the water; it is then transferred to the treatment vats below, where leaching is completed. The aeration thus secured is beneficial.

Caldercott's continuous-collecting system for sand consists in classifying with diaphragm cones and draining the thickened sand on a slowly revolving horizontal table, about 20 ft. in diameter, provided with a wide annular filter of coco mat and calico supported on wire screen. Here the sand is dewatered by a vacuum of about 5 lb. per square inch and removed by a fixed plough; it falls on a belt conveyor and is conveyed to the treatment vats.

**Leaching.**—The manner of applying solution varies. Gold dissolves rapidly, especially from fine sand, giving rich effluents in the early stages of leaching; the



value falling off rather rapidly; silver often dissolves slowly, showing less difference in the value of the effluents with time. For instance, a particular ore yielded 70 per cent of the extractable gold, but only 35 per cent of the extractable silver in the first quarter of the total effluent solution. Hence, by precipitating only the first half of the effluent, and using the later portions fortified in cyanide, for the early treatment of succeeding charges, the volume precipitated is minimized, so that it may be possible to make good extractions while precipitating not more than half a ton of solution per ton of sand.

The strength and the alkalinity of solution and the number of hours of contact must be determined to suit each case, and great saving may result from adjusting these conditions, and the degree of comminution of the ore, after the general treatment has been established.

When two solutions are used, the strong is generally applied first, and the weak is followed by wash water sufficient to displace it. The wash water and water in moist or water-crushed ore mix with the solutions to some extent, yielding "first and last drainings" of low NaCN content and low in precious metals. To preserve the volume of plant solution constant, these drainings, or low solution, are best precipitated separately and the barren run to waste. A slight saving is effected by using a buffer of this barren solution just before the wash water. Sometimes a little weak solution is similarly used before the strong; this is advisable if cyanicides have not been removed previously.

When dry ore is crushed in cyanide solution the final wash water must be regulated to make up the deficit in solution which would occur otherwise.

The "leaching rate" of sand is measured by the fall per hour in the surface of solution standing over a charge of saturated ore in the vat. Good extractions are usually obtained with leaching rates of 2 in. or more per hour; at 1 in. more care is necessary, and slower rates are generally dangerous, shortening the time of contact by reason of the longer washing period necessary. As the voids in settled sand are usually about 50 per cent of the volume, solution descends through sand at about double the surface leaching rate, and the hours required for displacement of solution by wash water may be approximated by dividing twice the surface rate into the inches depth of charge.

With sand of given character, the leaching rate is not much retarded by a moderate increase in depth; the effect of depth is largely offset by increased head. An extremely thin layer of slimy material may, however, affect the rate profoundly. Application of a vacuum beneath the filter bottom was formerly practiced, when classification was usually imperfect; while increasing the flow it tended to cause packing of the charge and lower the normal leaching rate; it may be used with advantage in the final washing stages.

Solution may be supplied continuously to the charge, or may be added at such intervals as to allow the surface to become drained and thus entrap air. Solution is sometimes circulated repeatedly through a charge by an air lift or pump returning it from the bottom to the top; this gives the desired aeration, but the ultimate removal of precious metal is retarded. Maceration or soaking by closing solution outlets for long periods is an obsolete practice, but a too rapid flow should be controlled to avoid precipitating unnecessary solution.

**Tanks.**—For economy of material a round tank of uniform thickness should have a depth equal to one-half the diameter; for economy of hoops the shallower the better; for economy of foundation the reverse. A common compromise is to make the depth one-fourth to one-sixth the diameter. In steel vats the bottom

is usually at least  $\frac{1}{16}$  in. thicker than the sides; these also may be lighter toward the top. Steel tanks are riveted and have a ring of angle steel surrounding the bottom; a similar ring is often used at the rim, and deep tanks may be stiffened by a ring of T-iron or a channel section round the middle. For wooden tanks, round iron or steel hoops are preferable to flat ones, which often develop rust on the under side. To get the full strength, the ends should be suitably upset before threading, and the section at bottom of thread considered in calculating strength. For sizes requiring over  $1\frac{1}{8}$ -in. round it is preferable to use  $1\frac{1}{8}$ -in. or larger square steel. The sizes may increase by  $\frac{1}{8}$  from  $\frac{1}{2}$  in. at top, and the spacing be made correspondingly closer as depth increases. Heavy hoops and rings must be rolled to the proper curvature before use, and hoops must be provided with properly designed couplings.

In calculating the necessary cross-section of hoops or thickness of side, wet sand, like slime pulp, must be considered as a perfect fluid, as there are times when it is dangerously near that condition. Settled sand may be assumed to have 50 per cent voids, when the specific gravity of the wet mixture  $p$  is  $0.5(d + 1)$  where  $d$  = specific gravity of dry sand.

$D$  = diameter of tank in feet.

$H$  = depth from top to center of ring (or hoop) considered, in feet.

$p$  = specific gravity of pulp (=  $0.5(d + 1)$  for wet sand).

$t$  = thickness of steel vat in inches at depth  $H$ .

$W$  = inches width of ring controlled by hoop in wood vat at depth  $H$ .

Strain on square inch cross-section of steel sheet =  $\frac{2.6DHp}{t}$  lb.

Total strain on cross-section of hoop =  $2.6WDHp$  lb.

Thus, with a steel tank 50 ft. in diameter, the metal  $\frac{3}{4}$  in. thick at a depth of 10 ft. when filled with wet sand of specific gravity 2.8 ( $p = 1.9$ ) stands a strain of

$$2.6 \times 10 \times 50 \times \frac{1.9}{0.25} = 9,880 \text{ lb. per square inch}$$

Similarly with a wooden vat under the same conditions, a hoop 10 ft. from the top, spaced 6 in. from adjacent hoops, is subject to a strain of

$$2.6 \times 6 \times 10 \times 50 \times 1.9 = 14,820 \text{ lb.}$$

and for a factor of safety of 5, the hoop must be capable of standing 74,000 lb.

**Leaching in the Filter-press.**— This includes collection and complete treatment in the press, and usually requires solution to be applied under a pressure of at least 30 lb. per square inch. Separated slime or all-slimes ore, suitably thickened, is fed into the press by gravity, montejus or pump, until filled. Alternate plates are then connected with compressed air and the water displaced. Solution is next applied through the same channels, and leaching (which may involve several solutions and may be alternated with air treatment) is continued as long as gold dissolves; it is then displaced by wash water and the solid is finally discharged.

The Dehne press, used in Western Australia for roasted ore and in some cases for raw slime, was opened and discharged by hand; it did not differ essentially from the ordinary plate-and-frame press. Treatment was completed in some cases in a 2- or 3-hr. cycle, but operation was expensive, even when opening and closing were effected by hydraulic power, and it was generally found preferable to dissolve the gold in agitators and use the press for filtering and washing only.

The Merrill press discharges the solids by mechanical sluicing through a bottom channel provided with ports, making it possible to use a press continuously for many

months without opening or changing cloths. Sluicing is effected by a series of nozzles in a rotating pipe or bar running the full length of the press, it requires 3 to 5 tons of water per ton of solid, depending on the character of the latter; much of this water may be recovered if desired by a thickener or rotary filter. While the first cost of this filter is comparatively high, the treatment requires a minimum of labor. With granular slime, a 4-in. frame is suitable; if extremely fine or flocculent, a 2- or 3-in. cake is preferable. Center washing may also be used, in which case the cake is not made to fill the frame completely, and air and solution are applied through the central opening in each cake instead of passing crosswise through the frame. In this case the cake is loosened by applying air for a short time behind the cloths prior to sluicing.

Leaching in the press is essentially similar to gravity leaching of sand, but much more rapid, occupying hours instead of days. For instance, with Homestake ore, the coarser mill sand yielded 70 per cent of its gold by leaching in a 7-day cycle; if reground this yield increased to about 80 per cent, the finer portions of the sand yielding 90 per cent. The slime and fine sand treated in the Merrill press yield 90 per cent in a cycle of 8 to 10 hr., of which 1 hr. is consumed in filling and one in sluicing. The operating cost in each case is about the same.

The Sweetland press has a cylindrical shell, opening by a hinge, the circular plates being tipped for discharge.

**Simple Decantation.**—In this process of slime treatment the material was agitated with cyanide solution and allowed to settle, the clear supernatant liquid was decanted off by a swinging pipe or flexible hose supported by a float which kept the inlet near the surface. This liquid was replaced by barren or low-grade solution or water; mixing, settling, and decantation were then repeated, and the same cycle might be repeated several times. The first decantate was always precipitated, sometimes the second or third, and the barren solution used with later decantates or washes for the make-up on a succeeding charge. The thickened residue, including more or less low-grade solution, was finally run off to a dam, or in some instances filtered. Some liquid separated on the dam and was sometimes pumped back for use in washes.

Successive agitations were carried out in the same vat—using mechanical agitation often aided by air—or, in a series of vats, one for each stage. In the latter case time was saved by hydraulicking the settled slime with solution or running it by gravity into a vat already containing solution, or, if the vats were on a level, a centrifugal pump was used with arrangements for drawing in a certain proportion of air for oxidation. Lime was commonly added to facilitate settling.

The process was adaptable to existing shallow vats by addition of an arm or paddle agitator. In South Africa, large shallow vats were used with bottoms slightly coned, but it was found that with increased depth, air agitation could be advantageously substituted, and this led to the development of the extremely deep Pachuca tank by F. C. Brown at Komata Reefs, New Zealand, in 1902.

The Pachuca may be from 10 by 30 to 15 by 45 ft., with a central air lift one-tenth the diameter, and a cone bottom inclined 60 deg. In addition to the lifting air, a second small pipe was added for stirring settled slime, and later a spider or movable set of radial pipes surrounding the air lift for the same purpose. The air outlets were valved or covered with flexible rubber to prevent entry of slime when the air was cut off.

At Waihi the Brown vat was used for crushed ore in connection with the Moore filter; at Goldfield and Treadwell it was used for fine-ground concentrate, and the final removal of solution was effected with a Kelly filter press.

**Continuous or series treatment** (not to be confused with countercurrent) was first used by Grothe and Mennell in 1908. The cyanide pulp is transferred through a series of three to six Pachuca tanks, maintaining it in agitation, thus saving the time occupied in emptying and filling, settling and stirring, and avoiding loss of head, except a few inches between successive tanks. The connecting pipes between adjacent tanks are set at a downward angle of about 60 deg., with an intermediate section of rubber hose. After leaving the agitation system the pulp passes to a suitable filter, an intermediate storage tank being usually provided in advance of the Moore and Butters filters, which have been much used. This is unnecessary with rotary filters which are automatic and almost equally effective.

By keeping the outlet at a suitable distance from the surface any considerable accumulation of sand is prevented; a certain accumulation of sand in the system is desirable, giving the coarser particles a longer treatment time than the average. Shallower agitators, as the Dorr, Trent, Parral, etc., may be used; the discharge may also be selected by other means. Short circuiting of some particles must inevitably occur, but in a series of tanks the probability of this is decreased.

The intermittent vacuum filters (Moore, Butters, etc.) and pressure filters (Burt, Kelly, etc.) require more attention, but are more flexible in application, as treatment can be completed in them, as well as washing and dewatering; rotary vacuum filters (both the drum type, Oliver, and Portland, and the American or disc type), are practically restricted to washing and dewatering. Dewatering may be carried by any of these filters to about 25 per cent moisture.

In the Kelly system the agitators are followed by two sets of rotary washing filters in series; the cakes discharged from the first set are re-pulped with wash solution or water in intermediate mixers to a liquid ratio about 1:1. The loss of dissolved value in the final cake is thus minimized.

**Continuous Countercurrent Decantation**, an adaptation of a well-known principle,<sup>1</sup> was attempted in cyaniding by Randall (South Dakota) in 1901, and by Denny (South Africa) in 1903, using cone-shaped agitators. It was made a practical success by the application of the Dorr thickener, a series of three to five of these being used, together with a number of agitators, the ore being usually crushed in solution.

After leaving the first thickener, the partly thickened pulp passes through the group of agitators, which may be in series or series parallel, and then through the remaining thickeners, and is discharged with or without filtration. By setting the last thickener highest, and the others in steps leading to it, the decanted solution flows back by gravity in the opposite direction to the solid, while the thickened pulp is transferred by diaphragm pumps. If on a level, the solution may be moved by air lifts. Excess

<sup>1</sup> The countercurrent principle allows the original ore to be treated with solution fairly rich in precious metal, but when partly exhausted, it must come in contact with poorer solutions, finishing either with wash water or with solution carrying only traces of value. The valuable content of the reagent should be as closely as possible proportioned to that extractable from the ore it meets.

An approach to this ideal is the conveying of crushed ore through a launder or horizontal pipe while a slow stream of cyanide solution travels in the opposite direction. Mere prolonged agitation, or the continuous passage of pulp through a series of agitators without a countercurrent, is entirely opposed to this principle, the solvent becoming enriched as the ore is impoverished.

In any continuous system the time an average particle remains in any thickener or agitator is found by dividing the weight of pulp passing hourly into the total weight of pulp contained in that unit. The arrangement (series or parallel) of any group of units does not, therefore, affect the average time occupied by the pulp in passing the group. Lengthening out the series of units decreases the probability of the rapid escape or short circuiting of any particle. (Cf. pp. 199 to 201, this book.)

solution from the first thickener is precipitated and returned to the second or third one from the end; cyanide is added to one of the agitators.

Points essential to success are: solution of the maximum gold or silver before leaving the agitator system, and efficiency of settling in succeeding thickeners—to at least 50 per cent solid if possible; in most cases, and always if the percentage of solid in effluents is under 50, the final discharge should be treated on a rotary filter to reduce soluble losses. Underflow solution is always slightly richer than overflow, owing to some dissolving and to diffusion of adsorbed or absorbed solution.

The flow sheet of United Eastern mill shows conditions prevailing with a pulp difficult to settle. Theory and practical applications are discussed by Eames,<sup>1</sup> Dorr and Dougan at Elko Prince,<sup>2</sup> and W. O. North at United Eastern.<sup>3</sup>

**Residues** may be discharged by sluicing where water is plentiful, and in some cases carried off by convenient streams, but more commonly require to be settled in dams. In some localities substantial dams must be built of concrete or masonry, or heavy timber, but it is more usual to construct the dam from the coarser portion of the tailing itself. Sometimes empty cyanide boxes or drums are filled with sand to form the initial wall, or cells of light woodwork are similarly filled, or the tailing itself is shoveled up to form a retaining wall. The sluiced tailing is then roughly classified in such a way as to deposit the coarser material near the dam wall, while the finer settles nearer the middle, where a steeply inclined or vertical overflow box may be arranged, the overflow level being gradually raised by adding slats when necessary. Where possible, it is convenient to have two or three dams or sections, one of which may drain and consolidate while another is in use, the more solid portion being then shoveled up to form the wall. A fair proportion of clayey material, or of contained lime, makes an excellent binder for the heavy sand, so that such dams may be built up on suitable slopes to a great height.

Sand residue may be removed by shoveling through bottom doors, or by a mechanical excavator, such as the Blaisdell, and carried off in cars, or by aerial conveyors, or by a conveyor belt which may deliver it to an elevating stacker. Slime, dewatered by a rotary or other filter, may be similarly carried off.

Or the tailing, sluiced or in cars, may be used for filling the stopes from which it originated; if more than a trace of cyanide remains, it may be necessary to decompose it by addition of permanganate.

Slime residues, thickened or settled without a filter, may usually be conveyed in pipes, but require a large area for satisfactory collection.

Water courses below residue dams are liable to contamination sufficient to cause the death of birds and animals unless due precautions are taken. Whenever possible, it is desirable to pump any accumulated liquid back to the plant as a matter of precaution, as well as of economy on account of contained cyanide and precious metal.

"Dissolved values" carried to residue dams behave differently according to climatic conditions. In arid regions evaporation takes place rapidly and salts effloresce at the surface forming a thin layer of much enriched material—in some cases worth \$100 per ton—which may be collected from time to time by careful sweeping or scraping, and returned to the plant. Where the rainfall is fairly heavy the surface is usually impoverished; in some cases reprecipitation takes place on organic matter near the floor of the dam, in others some recovery may be made by precipitating the seepage by zinc boxes or, if acid, by scrap iron.

Similar dams may be used for the storage of untreated tailing intended for subsequent treatment. These should be constructed with a view to the reclamation of the tailing, removing trees and other obstructions, leveling the bottom, and excluding organic matter when possible; sand and slime may advantageously be segregated.

<sup>1</sup> *Trans. A. I. M. E.*, 87, 142.

<sup>2</sup> *Ibid.*, 80, 84.

<sup>3</sup> *Ibid.*, 63, 548.

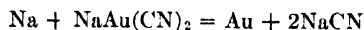
## PRECIPITATION

**Electrolysis** as a mode of precipitation attracted many inventors as it seemed reasonable to expect a large measure of regeneration. Siemens & Halske used multiple iron anodes and thin, sheet-lead cathodes, which were to be removed and cupeled after accumulating a suitable amount of gold; the current was of low voltage and a density of 0.04 to 0.06 amp. per square foot. The iron anodes were encased in hessian (burlap), but much Prussian blue and other by-products complicated the process, and the loss of iron was 0.3 to 0.5 lb. per ton treated. The main difficulty was the excessive electrode area and tank volume required approximately to exhaust a solution, the electrodes being 1 to 1.5 in. apart, and 20 sq. ft. or more in area.

Butters modified the process by using tinned iron cathodes and much higher current density; Andreoli invented anodes of lead coated with lead peroxide; Cowper-Coles used anodes of peroxidized lead and cathodes of aluminum, from which the deposited metal was to be stripped in sheets.

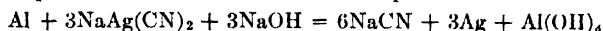
Several inventors attempted to precipitate the gold as an amalgam by using as cathode a layer of mercury or an amalgamated copper plate. Some filtered the solution, others attempted to precipitate on plates suspended in the pulp during agitation; some added common salt to increase the conductivity, but in no case was entire success attained. Pelatan and Clerici introduced several apparatus for this purpose, and others were devised by Riecken, Hendryx, Oliver, Mumford, Hebaus, and Noriega.

**Sodium and Sodium Amalgam.**—The ideal precipitant for gold and silver from cyanide solutions would be metallic sodium, completely regenerating the alkaline cyanide:



Attempts to use this reaction by means of sodium amalgam have not met with practical success. Molloy proposed to make metallic sodium by electrolysis of  $\text{Na}_2\text{CO}_3$  solution with a mercury cathode communicating with and diffusing into a body of mercury kept in contact with the cyanide solution; others sprayed sodium amalgam through a rising stream of solution, or kept it moving by means of amalgamated discs.

**Aluminum and zinc** stand next to sodium in the line of available positive metals, and have proved the most practical precipitants for gold and silver. Each replaces silver in solution, but aluminum forms no double cyanide and requires the presence of some free alkali. The equation:



indicates the complete regeneration of  $\text{NaCN}$  and the formation of alumina, which, however, dissolves in  $\text{NaOH}$  to form an aluminate, which may be assumed to be  $\text{NaAlO}_2$ . The  $\text{NaAlO}_2$  reacts with  $\text{CaO}$  in solution to form insoluble  $\text{CaAl}_2\text{O}_4$ . Gold is not readily precipitated by aluminum, unless a fair proportion of silver is present; mercury is, but copper is not precipitated.

Aluminum dust has been successfully used in silver mills at Cobalt; it is fed in a manner similar to zinc dust, but must be retained in a special agitating tank to increase the time of contact. Hamilton's system, in use at Butters' Divisadero plant, involves the removal of calcium by a minimum of soda ash prior to adding aluminum; the aluminum passing into solution being later thrown out by lime used in the mill.

Hamilton states that, in practice, 1 part of aluminum precipitates only 3 of silver in place of the calculated 12, the difference being mainly due to a reaction with NaOH to yield hydrogen. Alumina in precipitate makes refining difficult.

With zinc, the essential reaction is, similarly, a replacement of gold and silver, the zinc going into solution as double cyanide:



No regeneration is apparent, but the double cyanide thus formed has a marked solvent action on gold and silver, which is increased by the presence of free alkali up to a ratio of about 4NaOH for each molecule, or about two- and a-half times the weight of zinc. Precipitation is complicated by side reactions, especially the evolution of hydrogen by reaction of Zn with NaCN and NaOH forming additional  $\text{Na}_2\text{Zn}(\text{CN})_4$  and  $\text{Na}_2\text{ZnO}_2$  (zincate); this H further reacts to form sulphide by reduction of NaCNS and other sulphur salts, the  $\text{Na}_2\text{S}$  then precipitating Pb, Hg, or Ag as sulphide instead of metal. Some precipitation of Hg, Cu, etc. is due to direct action of zinc. Christy and others have written equations purporting to show a definite proportion between Au and H produced, but there is no fixed relation.

**Zinc shaving** was recommended by MacArthur and Forrest for a "metallurgical filter" after testing various forms of zinc. U. S. patent 418138 (1889) describes a vessel or series of vessels, with perforated false bottoms, carrying a sponge of "filiform zinc" cut by turning tool from a series of zinc discs, solution being arranged to rise through each section of a set of boxes or compartments.

Zinc boxes are made of wood or steel, occasionally of cement, sometimes in units but usually in a series of five or six similar compartments, each with a false screen bottom, the new zinc being added at the lower end and moved up as it disappears from the upper end. Each section usually has a plugged bottom hole communicating with a pipe or enclosed launder which leads to a tank or receiver for use at the clean-up; the top is often covered with coarse screen as a precaution against theft. At a clean-up, the fine material is shaken down and washed through the screen bottom, and drawn off or washed down to the receiving tank from which it is pumped to a small filter press. A considerable amount of precious metal is held back by the residual zinc moved to the head compartments. Some "short zinc" often has to be separately treated. It is advantageous to increase the space beneath the false bottom of the head compartments. The actual zinc-filled space usually recommended is one cubic foot for each ton of solution daily precipitated, but in practice it may be from one-quarter to double this. Five compartments are usually sufficient, but it is advisable to keep an empty compartment at the tail end.

Suitably packed, a cubic foot of fine zinc shaving weighs about 6 or 7 lb. but the coarser material used for silver may weigh 14 lb. It is now made by soldering together sheets of rolled zinc, coiling this closely on a roller or mandrel which is then set in a lathe, and cut by a chisel making an oblique cut at the ends. It is desirable when cutting to wind the thread into hanks of a size to fit the boxes in which it is used.

If the shaving is assumed to be a continuous rectangular strip of width  $a$  and thickness  $b$  in., the surface exposed by 1 lb. of zinc is

$$0.053\left(\frac{1}{a} + \frac{1}{b}\right) \text{ sq. ft., or nearly } \frac{0.055}{b} \text{ if thin.}$$

If the section is not rectangular, but a parallelogram of angle  $A$ , this must be multiplied by  $\text{cosec } A$ .

**Zinc dust** as a practical gold precipitant was first used by Sulman at Deloro, Ontario, added intermittently to a rising stream of solution in an inverted cone,

and passing to a filter. Later Waldstein and others added it by sprinkling it dry or as an emulsion in large charges upon vats of solution in a state of agitation, which were then pumped through square filter presses. Merrill introduced the practice of feeding it continuously to a moving stream of solution and using a triangular filter press; this system is now in use at nearly all the larger plants on the American continent, and is gradually displacing shavings elsewhere.

Feeders of several types are in use. One of the best is a slow-moving horizontal belt, on which a charge sufficient for several hours is spread in a uniform layer; this falls into a small mixing cone through which a trickle of auxiliary solution conveys it to the pump suction pipe. Another is a hopper at the outlet of which revolves a roller or pulley which removes a narrow ribbon of dust, the thickness of which is regulated by an adjustable slot. ✕ the zinc may be removed from the hopper by an auger-like horizontal screw. These feeders require a jarring mechanism to prevent the dust from adhering or bridging. Sometimes a miniature tube mill is added as a mixer. For accurate measurement it is convenient to have duplicate tanks of 100 or 200 tons capacity, which are precipitated alternately, but a large single tank may be pumped continuously while solution flows into it.

Abandoning air agitation effected a considerable saving of zinc, but the most marked improvement in precipitation has been the Crowe process of removing air from the solution by passing it through a vacuum tank on its way to the pump and just before introducing the zinc. In precipitating gold, the practical minimum of zinc dust is now between 0.1 and 0.05 lb. per fluid ton, or 25 to 50 parts of zinc per million of solution. When starting a press after a clean-up, it is advisable to add 50 per cent or more dust in excess of the normal charge, this is gradually diminished in successive charges until the regular amount is reached.

If zinc dust consists of equal spherical particles of diameter  $d$  in, 1 lb. exposes a surface of  $\frac{0.165}{d^2}$  sq. ft., and contains  $\frac{7.544}{d^3}$  particles. At an average diameter of  $\frac{1}{10,000}$  in, 1 lb. exposes 1,650 sq. ft., and 0.1 lb. spread through a ton of solution gives some 13,600,000 particles to the cubic inch.

For complete reaction 1 unit weight of Zn precipitates 6.03 units Au, 3.30 Ag, or 1.93 Cu', but the efficiencies obtained in practice are often extremely low, sometimes only a fraction of 1 per cent with low-grade gold solutions; with rich silver solutions 50 per cent may be reached, if complete exhaustion of the solution is not aimed at. Gold solutions can usually be precipitated with zinc dust to within 1 cent per ton, with a less expenditure of zinc than shavings require.

The best zinc dust was formerly imported, it usually contained about 2 per cent lead and often some cadmium; a much more efficient dust is now made in the United States, practically free from foreign metals and extremely uniform in size, the finer grades nearly all passing a 300-mesh sieve. It invariably contains oxide, often between 5 and 10 per cent ZnO, but this is not visible under a microscope which shows uniform bright spherules. The thickness of a surface layer of 10 per cent ZnO on spheres would be less than one-fiftieth the diameter. Extreme fineness is advantageous with low-grade gold solutions, but not necessary with the higher metal concentrations obtained from silver ores.

With zinc dust, 1 sq. ft. net filter surface suffices for 1.5 tons (or 50 cu. ft.) solution per day, or 6 tons per hour per 100 sq. ft.; with clear solutions a press may be run for long periods at double this rate. Colloidal suspended matter soon increases the pressure and reduces the pumping rate. For gold solutions 2-in. distance frames are suitable, 3- or 4-in. for silver. On opening a press most of the cake falls into the wheeled tray placed beneath; the remainder is easily removed by scrapers.



The practical efficiencies obtained with zinc dust, and the accumulations of zinc in solution, have averaged about the same as with shaving.

The dust process involves a more expensive installation than zinc shavings, but has the advantage of greater compactness and cleanliness, and involves less labor in maintenance and cleaning up as well as less risk of theft. The periodical clean-up is absolute, while a holdover of several thousand dollars' worth of precious metal commonly occurs with zinc shavings, and makes it impossible to compare the actual with what is often called the "theoretical" recovery. After a destructive fire, precipitate in a filter press has been found intact, while zinc boxes have entailed great difficulty in the attempts to recover their contents. At a gold plant a press occupying a floor space of 5 by 14 ft. can easily carry a month's accumulation of \$40,000.

The comparative cost of the two systems at any time depends, of course, upon the wage scale and the relative prices of zinc dust and spelter. The Crowe process effects an economy in both.

Zinc in other forms has occasionally been used as a precipitant, such as small discs, slugs or balls in a rotating cylinder or pan through which solution passed.

**Sodium sulphide** ( $\text{Na}_2\text{S}$ ) does not appreciably affect gold or copper in cyanide solution, but precipitates silver as  $\text{Ag}_2\text{S}$  from  $\text{NaAg}(\text{CN})_2$ , at the same time regenerating  $\text{NaCN}$ , and carrying down some gold in the presence of a large proportion of silver. Owing to the reversibility of the reaction, precipitation must either be imperfect or a slight excess of  $\text{Na}_2\text{S}$  must remain in solution, which is an objection to its use, as is also the necessary further treatment of the precipitate. It was patented by Janin and Merrill in 1894, but was not used until adopted at Nipissing as a substitute for the expensive aluminum dust. The precipitate is here reduced to metal by the Denny process, by contact with slugs of aluminum in a tube mill.

**Carbon as a Precipitant.**—Graphite has no precipitant action whatever on gold or silver in cyanide solution, nor has wood fiber (cellulose). Charcoal, partly burned or charred wood, some varieties of decaying wood, and some of the carbonaceous material found in certain black or "graphitic" shales and slates, all precipitate gold from its solutions, some of them rapidly, and in some cases they may prevent its solution. Freshly burned charcoal is most energetic; after long storage it is much less effective, but the precipitating property may be largely restored by reburning. It is usually assumed to be due to occluded gases ( $\text{CO}$  or  $\text{H}$ ) but nothing has been definitely determined on this point; these gases and the hydrocarbons in their ordinary form are quite inert. Coke and some varieties of coal have some precipitating effect, and in South Africa Caldecott patented the use of partly burned coal as a precipitant. In Australia, charcoal has been used to some extent as an actual precipitant, but the large volume required makes it inconvenient, and the final recovery of the gold is troublesome. Silver also is less completely precipitated.

The discovery, during the late war, of means of activating charcoal, and the known high activity of coconut shell and other dense charcoals, and of kelp char, and the fact that fresh pine charcoal is almost equally effective as a gold precipitant, all suggest that charcoal has some practical possibilities if a better mode of application is discovered. Agitation with finely powdered, recently burned charcoal followed by filtration gives promising results on the small scale.

Edwards at Yuanmi, Western Australia, used three Butters-type vacuum filters in series, each of 260 sq. ft. surface and charged with 300 lb. of ground charcoal; this system precipitated 280 to 420 tons daily, leaving 7 to 8 cts. gold in solution out of

an original \$3.25. One filter was renewed every three days, making consumption  $\frac{1}{4}$  to  $\frac{1}{2}$  lb. per ton. The dried product was burned and the ash fluxed in crucibles with borax, sand, and salt.

**Refining.**—Dry cyanide precipitate may contain up to 70 per cent metallic zinc or ZnO; that obtained by zinc dust from gold ore averages about 25 to 40 per cent, that from rich silver ore much less. If precipitant and solutions were lead free, precipitate from rich gold or silver solutions may be melted directly in crucibles with borax; it is more commonly acid treated to remove zinc or sometimes toasted in iron muffles as a preliminary step. The removal of zinc by distillation in Faber du Faur furnaces has been used experimentally.

Borax is the most important flux, best used as crushed borax glass; the crystals contain 50 per cent of water. Soda ash and silica are also useful, depending on the impurities to be fluxed off; bicarbonate is sometimes used in place of soda ash, though more expensive and less efficient. Niter or sodium nitrate may be used to oxidize zinc, sulphides, etc.; manganese peroxide may be substituted, as it gives off oxygen more gradually; oxidizing agents attack graphite crucibles, and also tend to carry silver into the slag. Clay liners may be used to protect the crucibles. Fluorspar helps to maintain fluid slags. Litharge is used only when cupellation is the final step in the refining process.

Lead present in zinc or added to solutions appears in precipitate as metal or PbS, and sulphuric acid removes but little of it. Acid treatment, if followed by thorough washing, removes most of the zinc and calcium, and part of the copper. It is carried out in a lead-lined tank with a mechanical agitator, water being first introduced and strong acid added gradually to prevent boiling over. A suction fan is necessary to remove fumes, especially HCN, H<sub>2</sub>S and AsH<sub>3</sub>; and care is also necessary on account of the hydrogen evolved. When action ceases, more water is added, the liquid is decanted upon a filter or through a small filter press, the precipitate is then transferred to the filter and washed, and finally dried to a stage where it can be handled without dusting. Sodium bisulphate (NaHSO<sub>4</sub>), a by-product of acid works, may be used as a substitute for sulphuric acid.

After acid treatment silica, cadmium, mercury, and some copper remain with the precious metals, and some CuSO<sub>4</sub> and ZnSO<sub>4</sub>; mercury may sometimes be profitably distilled off after adding lime or metallic iron to decompose HgS. On melting with reducing agents sulphates are deoxidized, yielding matte, which usually carries silver, as well as copper, lead, and iron.

Large crucibles, up to No. 400, may be used in tilting furnaces fired with oil, gas, or powdered coal; sizes 100 and smaller may be poured with hand tongs from wind furnaces using coke, etc. Electric heating has been but little used. In direct fluxing the cost of graphite crucibles is a serious item; melting may also be done without crucibles in tilting furnaces lined with carborundum or other refractory, or large crucibles may be set on a reverberatory hearth.

Rich silver precipitate is, at large plants, fused directly on a reverberatory hearth and tapped to molds; at Nipissing it is finished on the hearth by air-blast refining. United Comstock has an oil-fired tilting reverberatory.

The Tavener process, developed in South Africa, consists in mixing the precipitate with litharge and some sand, and smelting in a small reverberatory or pan furnace; the reduced rich lead is tapped off and cupeled.

At the Homestake, precipitate, raw or acid treated, is partly dried and briquetted after mixing with a flux of borax, borax glass, litharge, and a little silica. The briquettes are fused in a small English cupel furnace on a test of Portland cement (three-fourths) and limestone (one-fourth) which is started by adding a little lead;

the slag is tapped off from time to time together with some of the reduced lead. When all melted the surface is cleaned off and the lead cupeled on the same test, returning accumulated lead; the final slab of gold is broken up while still hot, melted in crucibles, and cast into bars. Low-grade precipitate is best briquetted, passed through a small blast furnace, and the lead cupeled.

The cupel slag, matte, and similar by-products, are treated in a small blast furnace, and the lead is either cupeled directly or used to start cupellation in the next run. The litharge from the lead processes is ground and used for flux at the next clean-up.

If the precipitate is briquetted and treated raw the increased losses in lead in slags, etc., offset any saving in acid. The holdover in blast-furnace by-product lead and litharge is less than 1 per cent of a month's run, and the only by-product to be marketed is the impoverished matte from the blast furnace.

In fluxing, 100 lb. of raw gold precipitate may give up to 100 or even 200 lb. of slag; after acid treatment and lead refining, about the same total of slag and litharge together, but the proportions vary greatly with the flux and condition of the precipitate.

At all plants large enough to justify the expense—treating, say, at least 400 or 500 tons daily—a small lead blast furnace is an excellent investment. Not only can the by-products of cyanide clean-ups—and if necessary the entire clean-up after briquetting it or setting it with some binder—be treated economically in such a furnace, but all sorts of by-products can be handled at intervals with little or no previous preparation, such as mill skimmings, rich pyrite, black sand, iron superficially amalgamated, old copper plates, sweepings, rich slags, crucible scrapings, etc. An important essential is to avoid charging finely divided material, or the blast may become choked and the furnace freeze. Fines must be briquetted or set with some suitable binder, such as water glass or acid.

In preparing cyanide precipitate for refining by means of a cupel or blast furnace, the expense is about the same whether a preliminary acid treatment is used or not; the use of acid effects an important reduction of the lead losses. If much zinc remains in the mass smelted, the slags become stiff from the presence of spinel-like compounds, and more lead must be left in the slag. If the washing of acid-treated precipitate is imperfect, sulphuric acid or sulphate of calcium or zinc remaining, the  $\text{SO}_4$  becomes reduced in the cupel or furnace and matte is formed.

In many cases the mixture of by-products is almost self-fluxing, requiring only the addition of a little limestone or assay slag to run freely. Fluorspar is sometimes useful in maintaining a fluid slag. In the final furnace by-products, such as matte, slag, and litharge, the ratio of silver to gold is generally much higher than in the bullion bars.

**Air and Oxygen in Cyaniding.**—The oxygen necessary to dissolve gold is supplied by air dissolved in the solution, which is slightly less than that carried by an equal volume of water. Additional oxygen may be furnished in leaching by allowing solution to drain low before adding more, and thus entraining air; sometimes air is blown for several hours at a time through the filter bottom after draining a charge, and it may be similarly blown through charges of slime in the filter press.

In slime treatment, air thus serves a double purpose, being used as a mechanical agent in agitation or air lifting, as well as to aid solution of gold; when transferring pulp by centrifugal pumps air is sometimes admitted at suitable openings, and one of the advantages of the "double treatment" of sand is to admit air freely.

The oxygen required for actual dissolving of gold is small in quantity. Assuming the interstitial space in sand as 50 per cent, the solution contained in a ton of saturated sand (specific gravity, 2.6) would suffice to dissolve over \$50 in gold or 1.5 oz. of

metallic silver, were it not used up by reducing agents, but to oxidize these reducing agents (mainly ferrous and sulphur compounds in ore, or organic matter introduced) a large volume of additional air must be supplied. In precipitation, the presence of O is undesirable; see under Crowe Process. Deep agitators and pressure filtration favor the dissolving of O, while vacuum treatment removes it from solution.

Excessive use of air is undesirable, as it carries off some HCN due to hydrolysis of NaCN, but free alkali almost entirely prevents this. The CO<sub>2</sub> in atmospheric air also tends to decompose NaCN; the CO<sub>2</sub> in 1,000 cu. ft. of free air at sea level will decompose about 0.1 lb. NaCN, or consume 0.06 lb. of CaO, yielding over 0.1 lb. of CaCO<sub>3</sub>. It may be removed by washing the air with caustic soda or lime water. Accumulation of CaCO<sub>3</sub> on cloth gradually reduces its permeability; this is partially restored by treatment with dilute HCl, but each successive acid wash leaves the cloth a trifle less effective than the preceding. Air from compressors usually carries oil, which produces an objectionable coating on filter press cloths; this oil may be excluded by passing the air through a special filter press of a few large frames.

At sea level and freezing point, 1,000 cu. ft. of dry air contain 18.65 lb., 8.6 kg., or 272 troy oz. of oxygen. But at ordinary ranges of temperature and atmospheric moisture the O actually present is between 90 and 95 per cent of these weights; at higher altitudes the weight of O per 1,000 cu. ft. is directly proportional to the lower barometric pressure. It is convenient to read this by a mercurial barometer, and to note that the pressure of a 1-in. column = 0.49 lb. per square inch, also that the barometer falls about an inch for each 1,000 ft. elevation from the normal 30 in. at sea level.

Barometer, inches mercury . . . . .	30	25.0	20.0
Approximate elevation corresponding . . .	0	5,000 ft.	10,000 ft.
Pounds per square inch . . . . .	14.7	12 25	9 80
Relative solubility of oxygen . . . . .	100	83 3	66.7

SOLUBILITY OF OXYGEN IN DISTILLED WATER WHEN EXPOSED TO AIR AT SEA LEVEL  
(WINKLER)

Temperature, Centigrade . . . . .	0	5	10	15	20	25	30
Temperature, Fahrenheit . . . . .	32	41	50	59	68	77	86
Oxygen, cubic centimeters per liter <sup>1</sup> . . . . .	10.2	8.9	7.9	7.0	6.4	5.8	5.2
Oxygen, milligrams per liter <sup>2</sup> . . . . .	14	12.7	11.3	10.0	9.15	8.15	7.6

<sup>1</sup> From an atmosphere of pure oxygen the solubility is about 1.8 times this. Nitrogen from air dissolves at approximately double these volumes

<sup>2</sup> Multiply these weights by 0.002 for pounds O, and by 0.029 for troy ounces O, per ton of water.

For cyanide solutions, at sea level, it is safe to assume the solubility of O as over 90 per cent of that in water (MacLaurin found 87 per cent for 1 per cent KCN, 50 per cent for 10 per cent KCN) and at higher altitudes, to reduce this proportionately to barometric pressure. Thus at 5,000-ft. elevation the maximum solubility of O in ordinary solutions may be taken as about 8 mg. per liter or 8 parts per million, which is about 0.23 troy oz. per ton, sufficient to dissolve 5.7 oz. gold or 3.1 oz. metallic silver.

In working with deep tanks, and especially at high altitudes, it is important to remember that the solubility of oxygen varies with the absolute pressure (gage + atmosphere). In a slime tank containing pulp of specific gravity  $P$ , at a depth of  $H$  ft. from the surface, the gage pressure (pounds above atmosphere) =  $0.433 PH$ . Thus

in a Pachuca tank, 45 ft. deep, filled with pulp of specific gravity 1.2, the pressure at bottom =  $0.433 \times 45 \times 1.2 = 23.4$  lb. per sq. in.

If this is at an elevation of 5,000 ft., with barometer standing at 25 in. ( $25 \times 0.49 = 12.25$  lb.), the solubility of oxygen at the bottom will be nearly treble that at the surface.

$$\frac{23.4 + 12.25}{12.25} = 2.91$$

In working with thick slime the rate of solution of oxygen, like that of other substances such as gold or cyanide, is much diminished as compared with thin pulp or clear solution.

Solutions recently precipitated with zinc or aluminum, especially after vacuum treatment, are practically free from oxygen and nearly saturated with hydrogen, and, therefore, in the most unfavorable condition for dissolving gold; they should be given an opportunity to aerate by cascading, spraying, or agitation.

**Heating Solutions.**—Both the dissolution and precipitation of precious metal, as well as the settling of slime, are accelerated by a moderate rise in temperature, and systematic heating of solutions has often been proposed. It has been advantageously carried out with extremely cold solutions, or to assist in thawing frozen ore. Heating above 50 or 60°F. is, however, of doubtful value; as it diminishes the solubility of oxygen and favors decomposition of cyanide.

When exhaust or cheap steam is available, it may be led through coils or zigzag pipes near the bottom of solution tanks or sumps; conveying pipes and launders should also be protected from cold.

The settling of slime and filtering of solution through sand are also facilitated by heating, the rate of settling (and, therefore, the capacity of settling tanks, etc.) is inversely proportionate to viscosity of liquid. The settling rate of a slime is proportional to  $T + 10$ , where  $T$  = temperature Fahrenheit. Thus if a particular slime settles 18 in. per hour at 40°F., its settling rate at 60 will be  $\frac{60 + 10}{40 + 10} \times 18 = 25.2$  in. per hour. The same rule holds approximately for filtration rates.

In crushing ore, most of the energy applied to the machines becomes available as heat in the resulting pulp. As the specific heat of most ore and rock is between 0.2 and 0.25, that of solution being practically 1, it is easy to compute roughly the rise of temperature which may be expected. With low-water ratios it is often of importance as an insurance against freezing. One h.p.-hr. = about 2,550 B.t.u. and raises a ton of water about 1.25°F., or a ton of dry ore 5 to 6°F.

**Fouling of Solutions.**—In the earlier days of cyaniding much was said of the fouling of solutions, and it was necessary at times to dispose of "fouled" solution and make a fresh start. This is now rarely necessary; solutions are used continuously for many years without renewal and without material change in composition. The daily elimination of solution in residues, and in first and last drainings, is an appreciable percentage of the whole stock of plant solution, so that the solution is practically renewed every few months.<sup>1</sup> Zinc is removed to some extent by precipitation or adsorption on the ore or tailing.

<sup>1</sup> If  $p$  is the percentage of stock solution discharged daily, and  $x$  the percentage of any substance now present remaining in the system after  $n$  days

$$\log x = n \log \left(1 - \frac{p}{100}\right) + 2.$$

Thus, supposing 5 per cent of the stock is daily removed, only about 21.51 per cent of any material now in solution will remain after 30 days, 4.6 per cent after 60 days, less than 1 per cent after 90 days, etc. Hence, if any radical change is made in the treatment, such as substituting NaCN for KCN, the solutions soon reach practical equilibrium.

**Regeneration** of the cyanide usually lost as a solvent has proved an attractive field for invention, but so far has met with comparatively little success. The following lines have naturally suggested themselves.

1. Precipitation of precious metal by a metal simultaneously regenerating NaCN, such as Na directly, or Al indirectly, Zn itself has some effect, as its double cyanide is a feeble solvent, rendered more active by the presence of free alkali. Electrolytic precipitation may be included here

2. Oxidation of HCNS to  $\text{HCN} + \text{SO}_2$  or of  $\text{NaCNS}$  to yield  $\text{NaCN} + \text{SO}_2$ , the latter with alkali forming sulphate. This may be effected by electrolysis or by certain oxidizing agents, but the yield has always been disappointing, owing to decomposition of the product. In this connection reference must be made to the Clancy project.

3. Neutralization or acidification of solutions, on the one hand, yielding insoluble cyanides ( $\text{CuCN}$ ,  $\text{AgCN}$ ,  $\text{Zn}(\text{CN})_2$ ,  $\text{CuCNS}$ ,  $\text{AgCNS}$ , occasionally ferrocyanides), and on the other, liberating HCN. The precipitates must be separated to recover Au, Ag, and part of their contained CN by suitable means, the HCN may be removed at least partially from the solution by heat, by passing a current of air or gas, or by applying a vacuum as in the Crowe process. Gaseous HCN thus liberated may be absorbed in a suitable alkaline solution to form NaCN or  $\text{Ca}(\text{CN})_2$ , or the HCN in solution may be fixed by addition of alkali.

The general idea has been to operate upon "fouled solutions" or on the "low solution" normally and unavoidably thrown away daily in some form. The low concentration of solutions in general use has militated against the completeness of precipitation and volatilization.

**Filter Cloth.** Many varieties of filter cloth have been used in cyaniding ore, precipitation with zinc dust, and handling acid-treatment liquors. Cotton cloths of all the three common weaves—plain canvas with single or double thread, twill, and sateen—have been found satisfactory when the weight of material selected is suitable for the pressure and conditions of use. The more complicated weave known as chain cloth seems to have no sufficient superiority to justify its price. Paper is not generally to be recommended.

For precipitation it is convenient to use one of two systems (1) a fairly heavy cloth backing, covered with light "domestic" or twill, the latter to be removed at each clean-up and burned, or washed and reused once or twice, or (2) two layers of a medium-weight material, the outer to be removed at clean-up and either burned or washed for reuse. When reclothing, a new or washed cloth is put next the plate and the original undercloth replaced above it. Occasionally three or four thicknesses of very light material have been used, the outer layer being taken off at clean-up and a new one placed next the plate.

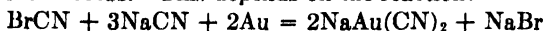
For filter bottoms of leaching vats a heavy canvas (such as No. 8 or 10-oz. duck) is desirable, and will last one to two years. It may be acid treated in place if the usual accumulation of calcium carbonate checks the leaching rate decidedly. A similar cloth may be used in filters of the Moore and Butters types, for slime presses a similar heavy canvas may be covered with a light or medium twill. These may similarly be acid treated by using hydrochloric acid, so highly diluted as to avoid attacking the iron frames.

The nominal "ounces" rating of canvas refers to the weight of a running yard of a standard width of 22 in., the "ounces" may be read directly by noting the weight in grams of a sample cut 4 by 7 in. (28 sq. in. or 180 sq. cm.). The "number" is approximately obtained by subtracting the "ounces" from 19. Thus if a sample of duck, 4 by 7 in., weighs 9 g., it indicates "9-oz." duck, or "No. 10." Figures thus determined

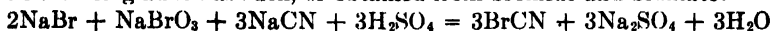
usually agree within one unit with the commercial ratings, but dealers occasionally apply the ounce rating to the square yard, making the nominal weight about 60 per cent too high. The present tendency is to specify weight per square yard, irrespective of the actual width of fabric.

### MODIFICATIONS OF THE CYANIDE PROCESS

**Bromocyanide Process.**—This depends on the reaction:



the BrCN being added as such, or obtained from bromide and bromate:



The bromocyanide process has been used in Western Australia, and to a limited extent in Canada and Colorado. An excellent resumé with bibliography is given by Stevens and Blackett.<sup>1</sup> Bromocyanide can be used to advantage only on two classes of ore: (1) Ores containing minerals such as tellurides, more soluble with this reagent than with plain cyanide; (2) ores requiring rapid dissolution of gold in order that other substances in the ore shall not have time to dissolve and foul the solution. A preliminary treatment with plain cyanide is always advisable. No appreciable amount of free alkali must be present. BrCN itself decomposes rather rapidly in solution and also induces wastage of NaCN. BrCN is itself rather expensive, and so are the mixtures from which it may be prepared (Br + NaOH + NaCN, or NaBr + NaBrO<sub>3</sub> + NaCN) and the "mixed salts" used for this purpose are liable to decomposition in storage. Cyanogen chloride cannot be substituted, and ICN is too expensive.

**Gitsham Process.**—Free HCN in presence of oxygen has a slight solvent action on gold. This process proposes to use feebly acid solutions, especially for ores containing antimony, copper, and other base metals. The effluent solutions are to be neutralized by lime before precipitation by zinc, and reacidified with addition of enough alkaline cyanide to bring them up to suitable strength.

**Gilmour-Young Process.**—This system was devised at a Nicaragua mine to utilize the existing Boss process pans for cyaniding rich ore. Copper amalgam was made by treating mercury with copper sulphate and iron filings, the squeezed product carrying about 15 per cent copper; zinc amalgam was sometimes added. A charge of dry ore was ground with cyanide solution, and about 200 lb. of mercury for 2 hr.; 30 lb. of copper amalgam was then added, and the whole ground 4 hr. longer, when the mercury was separated. The squeezed amalgam was enriched by repeated use and finally retorted, yielding bullion 700 to 750 fine.

**Diehl and Marriner Processes.**—These were evolved to treat the rich telluride ores of Western Australia. The Diehl process consists in wet crushing, sliming, and treatment first with KCN and then with BrCN in agitation vats and filter presses. The Marriner system involves dry crushing, roasting, amalgamation, and treatment of the roasted ore by percolation or by fine grinding and filter press. There were many modifications of each system in use; the results and costs did not differ greatly, as the cost of bromocyanide in one case offset that of roasting in the other. With the wet process concentration was often practiced, and the concentrate roasted preparatory to cyaniding.

**The Usher process** was an African slime method in which, after one stage of agitation, solution was introduced by multiple pipes over the bottom of a flat or cone-bottomed tank, and the upper clear portion continuously decanted for

<sup>1</sup> *Trans. I. M. M.*, 29, 290.

precipitation. Finally the slime was allowed to settle as usual. In one modification of the process umber, containing manganese peroxide, was used as an oxidizer.

The Denny desulphurizing process is used at the Nipissing Mine, Cobalt, to prepare silver sulphide ores for cyanidation. By grinding them in tube mills with ingots or slugs of aluminum and caustic soda, all silver minerals are decomposed, except dyscrasite, yielding metallic silver which is amenable to cyanide. At the same time  $\text{Na}_2\text{S}$  is formed, which can be used as a precipitant. The process is completed by agitating the pulp 12 hr. in a tank lined with aluminum plates.

**Antidotes to Cyanide Poisoning.**—The following materials should be kept at every cyanide plant and laboratory; sets should be placed at convenient points on every floor at which solutions are handled.

One sealed bottle (preferably a quick-opening "citrate of magnesia" bottle with rubber gasket), containing 1.5 g. of caustic soda ( $\text{NaOH}$ ) dissolved in 300 c.c. of water.

One sealed bottle (preferably a 2-oz., wide-mouth bottle with large projecting cork), containing 7.5 g. ( $\frac{1}{4}$  oz.) of ferrous sulphate crystals dissolved in 30 c.c. (1 oz.) of water. This water should be freshly boiled, and the vacant space in the bottle filled with carbon dioxide or hydrogen, to prevent oxidation; the cork must be completely covered with melted paraffin or sealing wax.

One corked tube containing 2 g. of finely powdered magnesia.

A large cup, of at least a pint capacity, preferably of white enameled ware, which will hold the three previous items, together with a spoon or flat stick for stirring them. When required, the ferrous sulphate is to be poured into the cup, followed by the soda and magnesia, and the whole well stirred and swallowed; no time should be wasted.

It is desirable to add a rubber stomach tube and a wooden gag, so that the antidote may be poured into the stomach of an unconscious patient if necessary.

These materials should be kept in a glass-fronted cupboard, easily accessible and conspicuously marked, and all foremen and shift bosses fully instructed in their use. The soda requires renewal after 2 or 3 years, as it slowly attacks glass. The ferrous sulphate also oxidizes slowly, but a small amount of yellow deposit may be ignored, as long as the solution remains strongly green.

The above is known as the Martin antidote, and was developed by Dr. C. J. Martin and R. A. O'Brien, of Melbourne, in 1902. Variations of the outfit have been put on the market by different dealers, but the equipment can be easily prepared at any laboratory. The essential reaction is the formation of ferrous hydroxide, avoiding any excess of caustic soda, and conversion of the cyanide into harmless ferrocyanide.

Among other remedies that have been suggested are: hydrogen peroxide (2 per cent solution used hypodermically and as a stomach wash), cobalt salts, adrenalin, sodium cacodylate, and silver nitrate (dilute solution followed by an emetic of salt water and mustard).

**Plant Precautions.**—An eczematous condition of the skin may be caused by long contact with strong cyanide solutions. This should be avoided at clean-ups of zinc boxes by greasing the hands and wearing rubber gloves in handling wet shavings; it is unnecessary to handle solution at other times.

Zinc shaving and dust, and aluminum dust, are decidedly inflammable. Caustic soda falling on zinc dust reacts with evolution of enough heat to ignite the liberated hydrogen and cause the zinc to smoulder. Extinguishers of the carbon-tetrachloride type must not be used on zinc-dust fires, as the reaction ( $\text{Zn} + \text{CCl}_4$ ) yields various irritating gases.



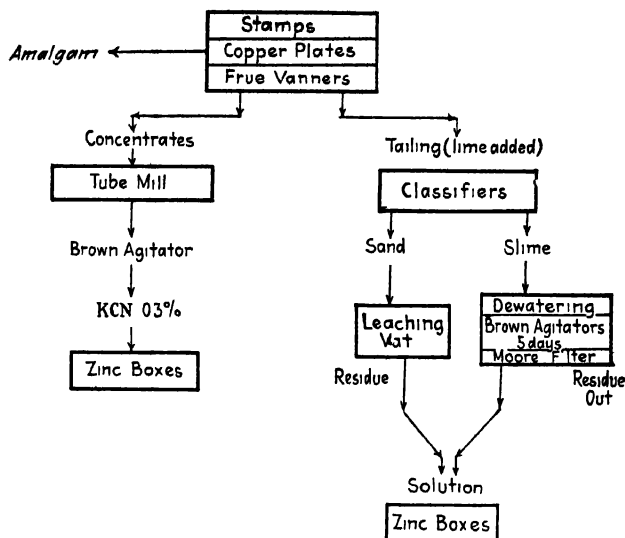


FIG. 5 Flow sheet Wulu mine New Zealand  
(For later flow sheet see *CHINESE Trans I M M* **24**, 400)

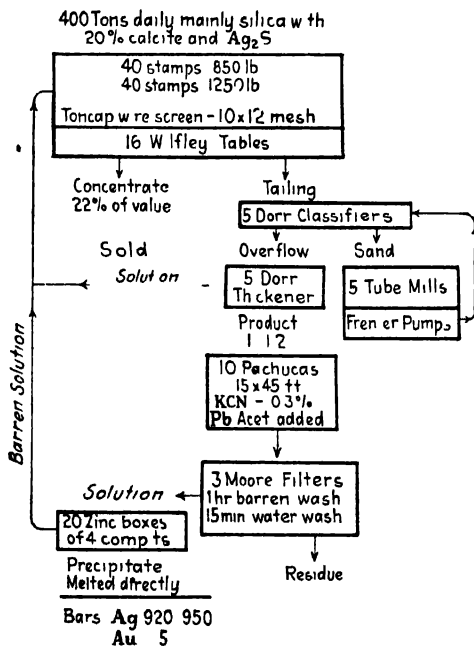


FIG. 6 Flow sheet San Rafael mine 1909  
(See GIRALDI *Cyanide Practice in Mexico*)

The reaction of acids with zinc precipitate yields, beside H, more or less  $H_2S$  and HCN, but a greater source of danger is the occasional presence of arsine ( $AsH_3$ ) in the gases liberated. This has been the cause of several deaths, and during acid treatment the gases should be carried off by a fan.

**Typical Operating Costs.**—The following are examples of costs of milling and cyaniding in various parts of the world. Comparisons are not of great value, being so largely influenced by local conditions, cost of transporting supplies, available power, etc., as well as the character of the material treated. In general, low costs are only attainable in the case of plants treating large tonnage without interruption. Daily tonnage is quoted where possible, and costs given in dollars per ton milled

Treadwell, Alaska, 1906		
Milling, concentration, amalgamating	0 25	
Concentrate treatment at smelter	0 14	\$0 39
1910 to 1911, Milling and concentrating		0 18
Wasp No 2, S. D., 1910, 400 tons, gold \$3 per ton, 68 per cent.		
Dry crushing (rolls) and cyaniding direct		0 65
Korea, 1910, 800 tons		
Stamp mill 0 58, cyaniding 0 18		0 76
Mysore, India, 1923, gold \$10 per ton, 97 per cent		
Milling, 0 42; tube mill and classifying 0 26, cyaniding 0 36		1 03
Waihi, New Zealand, 1910 to 1912, crushing in cyanide with forty stamps, tubes Pachucas, and filters of Moore type		1 51
Homestake, S. D., 4,200 tons gold \$4, 94 per cent.		
Milling 0 30, classifying and cyaniding 0 20		0 50
Elko Prince, Nev., 1917 60 tons, silver-gold		
All-slitting and countercurrent decantation		3 02
United Eastern, Arizona, 1917 to 1918, 250 tons, gold \$10		2 17
Rand, South Africa, 1906, average of several plants		
Milling 0 75, cyaniding 0 33, mechanical handling 0 14		1 22
Porcupine-Crown, Ont., 1914, 130 tons, gold \$20, 96 per cent		
Milling in solution, amalgamation, countercurrent decantation		1 23
Hollinger, Ont.		
Milling \$0 40, classifying and cyanide \$1		1 40
Nipissing, Ont., combined high- and low-grade mills,		
2 6 tons at 2,600 oz Ag, 99 per cent		
250 tons at 26 oz Ag, 92 per cent		
Milling 0 67, cyaniding 2 08		2 75
Tonopah, Nev., silver ore		
Milling and cyaniding, average 5 mills		3 00
Colorado, 1914 to 1915, 500 tons gold \$4		
Milling, concentration, cyanide		1 57
Western Australia, 1906, plants of 200 to 500 tons, telluride ore, gold \$10.		
Roasting, fine-grinding, cyaniding, filter press, average about		3 00
Raw treatment with cyanide and bromocyanide, average about		3 00
Mexico, mainly silver ores		1 50
Montana, 1901, 400 tons silver-gold tailing; cyaniding only		0 65
Treadwell, Alaska. Cyaniding concentrate, 1914, per ton concentrate		2 75

While the general tendency of recent metallurgy is distinctly in the direction of cyaniding in preference to other methods, and towards all-slitting and milling in solution, examples are not wanting which illustrate other methods and variations



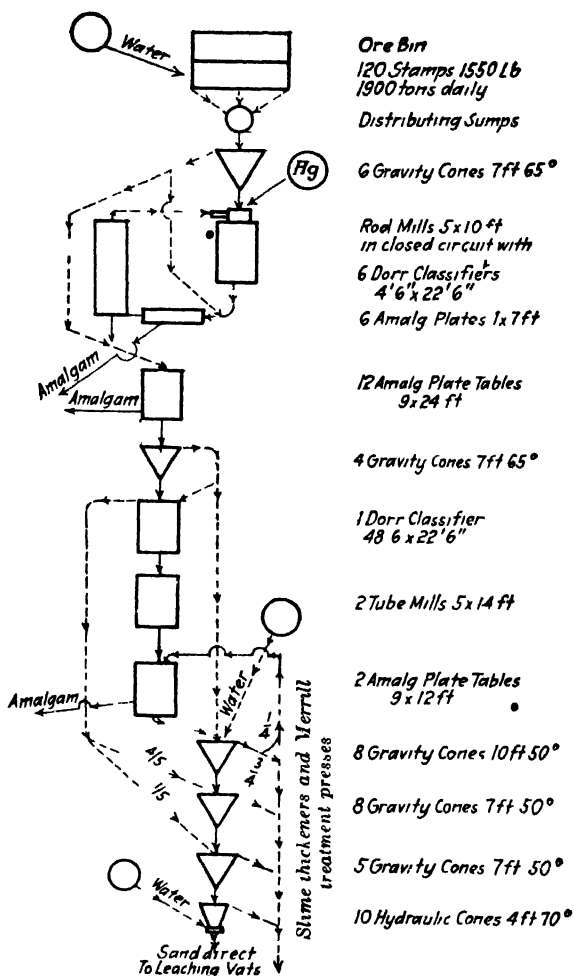


FIG 8 — Flow sheet, South mill, Homestake Mining (o, Lead, S, D). (A J Clark)  
(For cyanide treatment see Figs 14 and 15)

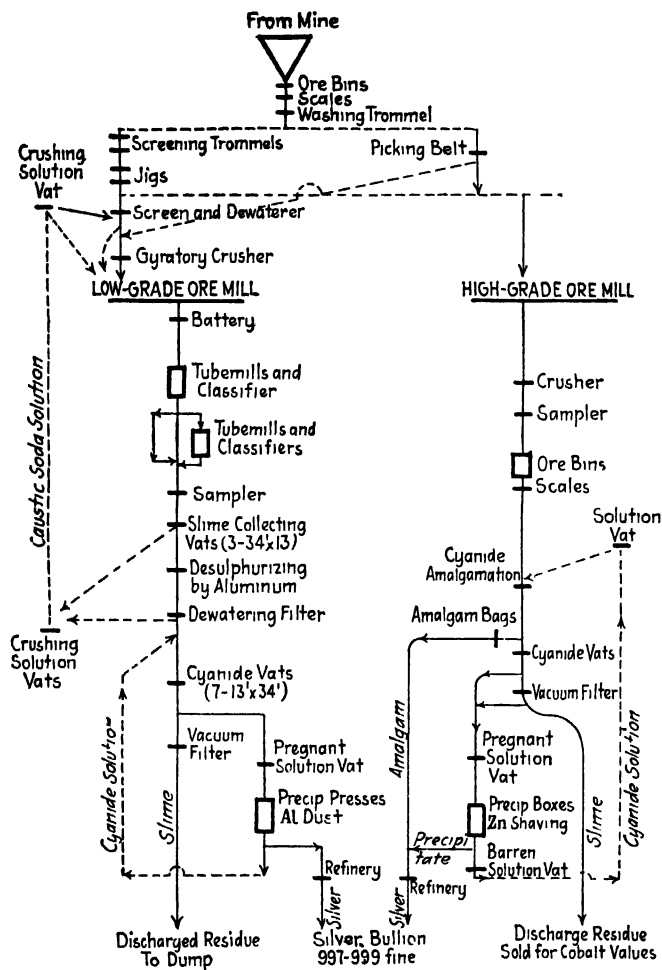


FIG. 9 —Flow sheet, Nipissing Mining Co.'s Mill.  
(See JOHNSTON, J, *Trans. A. I. M. E.*, **47**, 5)

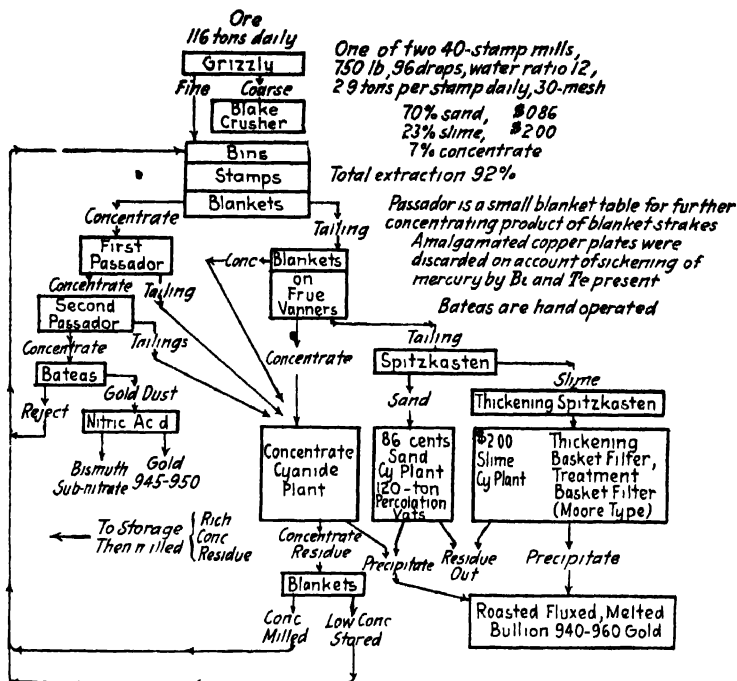


FIG. 10 Flow sheet Passagem mill Ouro Preto Brazil  
(See BENSUSAN, A. J. *Trans. I. M. M.* **20**, 27)

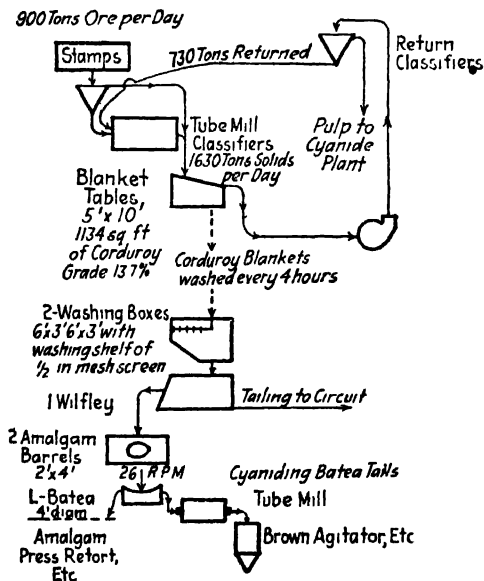
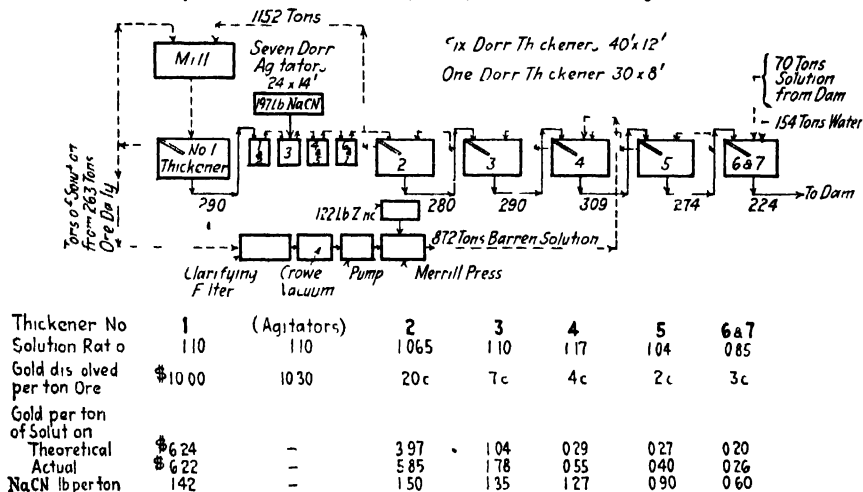


FIG 11—Flow sheet—corduroy blanket system, Modderfontein East, 1923.  
(See WARTENWEILER, F, *Jour C M M Soc So Afr*, Feb, 1923)

on Garfield and Wilfley tables, tailing discarded Primary concentrate retreated in two units, each with twelve Wilfleys

Lead concentrate retreated on 1 Wilfley		Middling Janney classifier, tube mill, Wilfleys		
Gold-lead concentrate, melted with iron		Rich-lead concentrate	Second lead concentrate	Pyritic tailing
Gold-lead bullion	Matte Shipped	Au \$100—\$800 Pb 50 per cent Shipped	Au \$400 Pb 40 per cent Ag 50 oz Shipped	Au \$1

Quartz-calcite ore with about 1 oz gold per ton, practically no silver Telsmith gyratory crusher  
Two 64 1/2 Marcy mills with Dorr classifiers in closed circuit  
Two 5x6 ft Allis Chalmers ball granulators with Dorr classifiers in closed circuit  
Six 40x14 ft, one 30x8 ft Dorr thickeners Seven 24x12 ft Dorr agitators in series  
Sodium cyanide 0.72% n No 1 thickener, 0.75 lb per ton added to No 3 agitator



The theoretical dissolved loss is \$0.17 per ton ore actual loss \$0.215 This seems high but nearly half of this is returned from dam as water A final rotary filter would reduce this materially

FIG. 12—Flow sheet, United Eastern 263-ton mill, Arizona  
(See NORTH, W O, Trans A I M E, 63, 548)

**Treadwell Group, Douglas Island, Alaska.**—The ore, averaging a little over \$2 gold per ton, was crushed in several mills aggregating 900 stamps of 1,020 and 850 lb, crushing about 5,000 tons daily through diagonal slot screens equivalent to 18 mesh. Each five-stamp battery was followed by 45 sq ft amalgamated copper plate and two Frue vanners. Tailing averaged about 20 cents, half the gold recovery was from plate, and half from concentrate, the latter was formerly treated by chlorination, but later shipped to a smelter.

Later amalgamation was abandoned, the pyritic concentrate (90 tons daily carrying about \$60 worth of gold per ton) was ground to 200 mesh by 5 by 22 ft. tube mills in closed circuit with Dorr classifiers, neutralized by lime, dewatered in Callow cones, and cyanided by agitation and repeated decantation in Pachuca tanks, 10 by 30 ft., residues filtered in Kelly pressure filters, solutions clarified in a special press and precipitated with zinc dust in Merrill presses.

The countercurrent principle was applied to the treatment; barren solution was used for the last agitation and successively used until the decantate from a first treatment carried about \$10 per ton, at which stage it was precipitated.

The densely packed, settled concentrate (specific gravity, 4.6 to 5) was successfully agitated by means of a "spider" supplied with compressed air and encircling

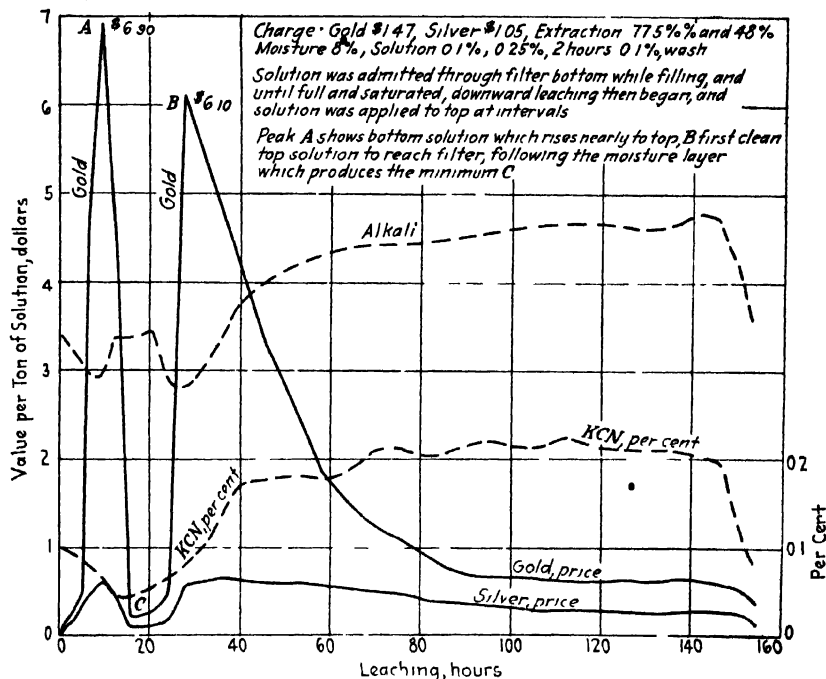


Fig. 13.—Leaching effluent uniform fine dust and Montana Mining Co., Marysville, Mont. Sec MERRILL & W., Eng. Min. Jour. 65, 459

the central agitation column of the Pachuca tanks<sup>1</sup> (cyaniding the concentrate yielded 96 per cent at a cost of \$3.25 per ton, against a total charge of \$11.95 per ton for shipping and smelting).

**Wasp No. 2 Mill, South Dakota**—The ore was a porous, oxidized "quartzite" (silicified sandy dolomite) requiring little stripping, and containing no cyanicides, carrying about \$3 worth of gold per ton. It yielded \$2 by leaching, at an operating cost of \$1 equally divided between mining and milling. The equipment was one No. 6, two No. 4 Gates crushers; four sets 14 by 36-in. rolls; screens with 4-mm. opening; six leaching vats, 32 ft. in diameter by 12 ft., holding 400 tons each. The ore was leached with 120 tons of strong solution (0.25 per cent KCN) and 350 tons of

<sup>1</sup> See KINZIE, *Trans. A. I. M. E.*, 34, 334; LASS, *Trans. A. I. M. E.* 42, 785



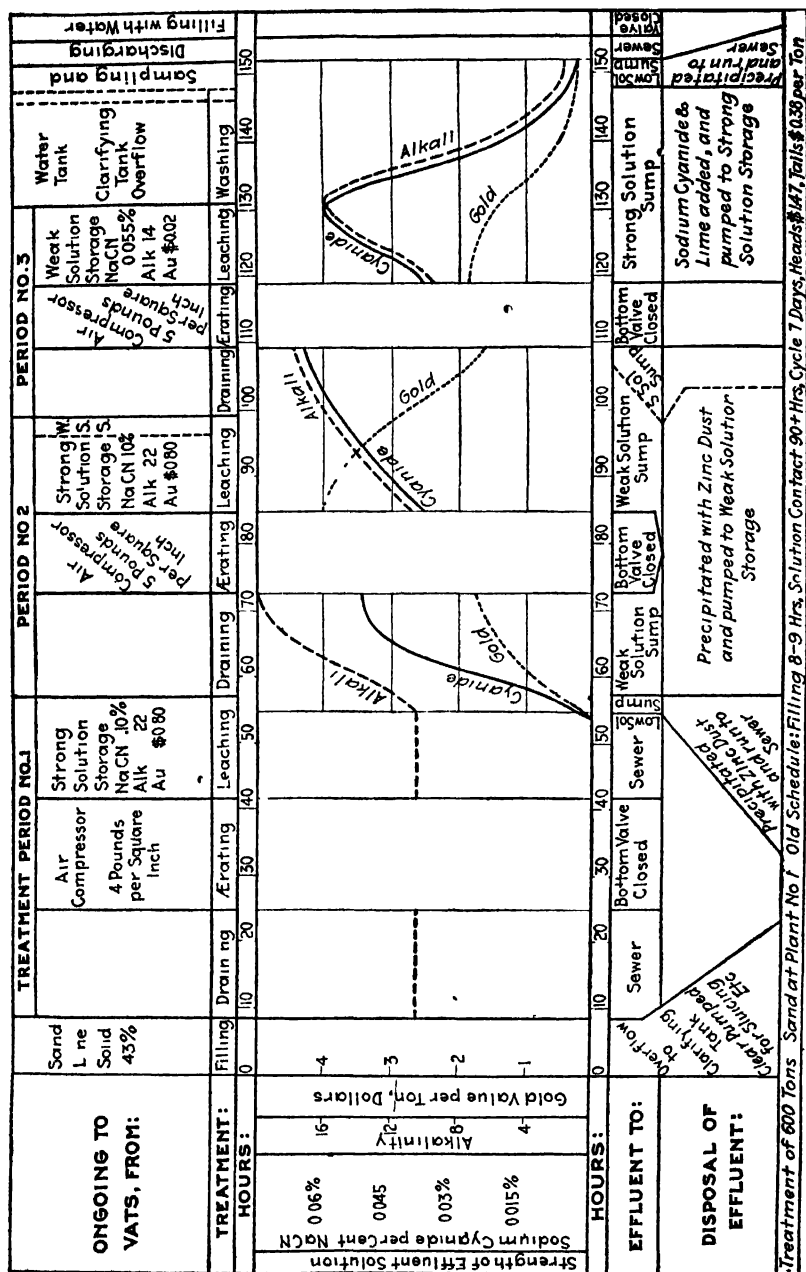


Fig. 14—Leaching at Homestake, South Dakota See CLARK and SHARWOOD, Trans. I. M. M., 22, 68

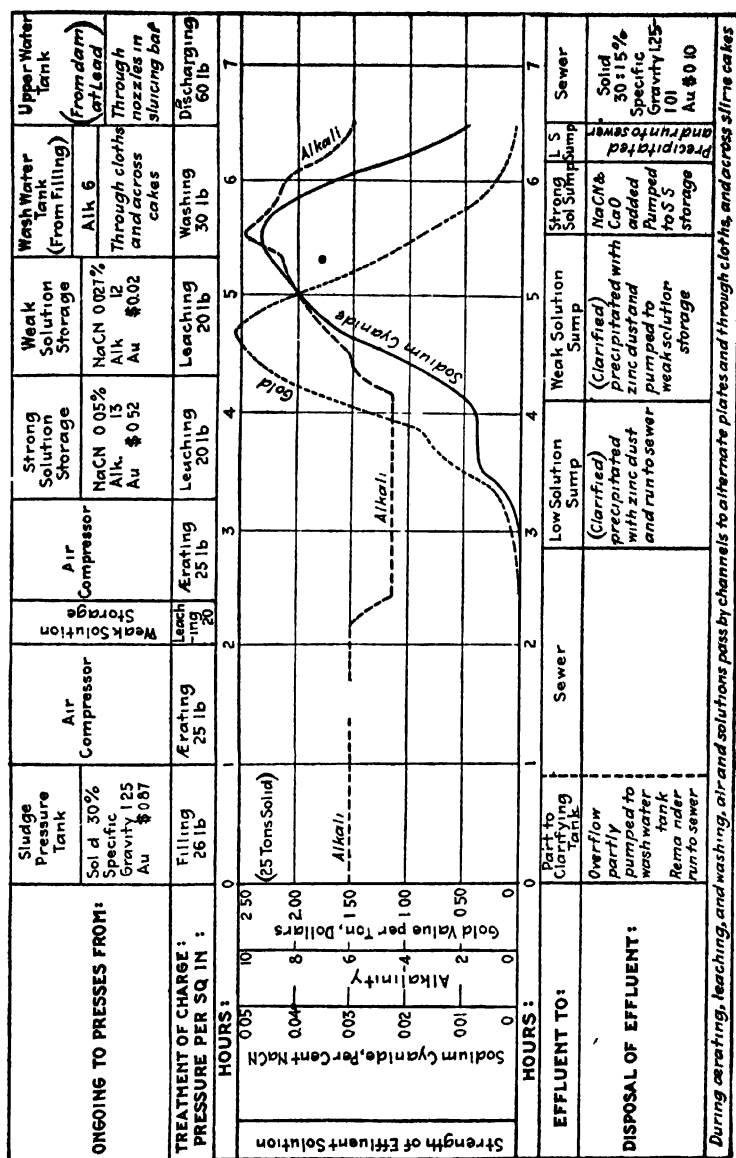


Fig 15—Slime treatment in Merrill filter-presses at Homestake, South Dakota See CLARK and SHARWOOD, Trans I M. M., 23, 68

weak solution (0.125 per cent KCN) and 50 tons of wash water; precipitating in zinc boxes 520 tons effluent, or 1.3 tons per ton ore; bullion fineness, Au 325, Ag 660. The residue was discharged by shoveling through bottom doors, and trammed to the dump<sup>1</sup>

**Intermittent Decantation** (Treating Accumulated or Dam Slime).—The material treated was a readily settling mixture of slime with extremely fine sand, from a settling dam, and contained approximately 20 per cent moisture. The tabulation shows average results for gold only for a month's treatment; the percentage of silver extracted was about 66 per cent of the gold figure. Treatment was completed in the same vats, which were 42 ft in diameter, with a central agitating shaft.

Period, 48 hr.; charges, 133 dry tons each; solvent (2.5:1), 333 tons (160 tons storage solution, 33 from moisture, 160 "wash" from preceding charges) originally 0.05 per cent KCN. At stages I and II the volume decanted off was exactly replaced by "wash" or water, and mixed by stirring with agitator and air

Period	Montana Mining Co., slime plant, hours treatment	Hours settling	Tons decanted	Tons decanted per ton solid	Per cent decanted of total solvent	Decantate	Gold per ton of decantate, cents	Gold decanted per ton of dry slime, cents
I	7 loading and mixing	15	215	1.60	64	I Precipitated	59	94
II	2 stirring and refill	11	202	1.52	60.5	II Precipitated	30	46
III	3 stirring and refill	8	185	1.39	55.6	III Carried over as wash to next charge	21	29
IV	2 discharging							

The gold value per ton of charge was \$2.20; the value per ton of residue, 66 cts.; calculated extraction, \$1.54 = 70 per cent; calculated precipitation, \$1.40 = 63.6 per cent; actual gold recovered, \$1.50 = 68.2 per cent.

When dissolved	Calculated loss of gold actually dissolved in above case, per unit	Recovery of gold actually dissolved, per cent	Recovery if 50 per cent decanted at each stir per cent	Recovery if 40 per cent decanted at each stir, per cent
I. First stir	$0.36 \times 0.395 \times 0.144 = 0.063$	93.7	87.5	78.4
II Second stir	$0.395 \times 0.144 = 0.175$	82.5	75	61
III Third stir	$0.444 + (0.063 \times 0.556) = 0.48$	52*	43.75*	37*

\* Somewhat increased in practice by recovery of a portion of the solution from period III by pumping back from residue dam

### MINOR AND OBSOLETE PROCESSES

**Chlorination Process for Gold.**—This was based on the fact that chlorine, in the presence of moisture, converts gold into the trichloride ( $\text{AuCl}_3$ ), which is soluble in water and removed by washing; the gold being then precipitated by ferrous sulphate, sulphur dioxide, hydrogen sulphide, or charcoal. Coarse gold requires long contact and should be removed by amalgamation. Pyritic ore or concentrate requires a dead roast before chlorination; thoroughly oxidized ore may be treated directly. Basic ores—containing lime and especially magnesia—

<sup>1</sup> See SIMMONS, JESSE, *Eng. Mining J.*, July 29, 1911, *Mining Eng. World*, Jan. 4, 1913.

absorbed much chlorine and might become heated. This was checked by roasting with a high temperature at the finish, to frit the magnesia with silica. Chlorination was suggested by Percy and by Plattner independently in 1848.

The *Deetken* or *California* process was carried out in comparatively small wooden vats with bottom filter of perforated boards, resting on slats and covered with coarse gravel and sand, a vat 8 ft in diameter with 3-ft staves would hold about 3 tons. The crushed and roasted ore was loosely charged by sifting in a moist condition to facilitate leaching, a cover was luted on with clay or dough, and gaseous chlorine generated in a lead vessel from manganese dioxide, salt, and sulphuric acid was admitted by a lead pipe to the bottom until it could be detected at a hole in the cover. In later practice, liquid chlorine was purchased in steel cylinders. After 12 to 36 hr contact (adding more chlorine if necessary), water was turned in at the top, any chlorine escaping at the bottom pipe being led to another vat. The yellow solution was run to the precipitating vat and the charge washed until the effluent was colorless. The residue was then shoveled out, if much silver was present it was transferred to another vat and leached there with hyposulphite solution. Some ores, rich in silver, were first leached with hyposulphite and then chlorinated.

The *barrel* process, used on a large scale in Colorado, involved the rotation of the ore in barrels of wood or heavy, lead-lined steel, holding 5 to 25 tons, while chlorine was generated under pressure in the mass by means of bleaching powder and sulphuric acid. Barrels were often built with an internal filter on one side, consisting of pebbles or coarse sand confined by slotted boards and a perforated lead plate. After 3 to 6 hr water under 20 to 40 lb pressure was admitted by a trunnion and washed the charge in 1 to 2 hr. A ton of ore would use at least 10 lb of bleach and 15 lb of sulphuric acid. The ore was charged dry from a hopper and discharged by sluicing through manholes in the side.

The *Munkitell* process consists in leaching the ore with two solutions, one of bleaching powder, the other sulphuric acid, which mix at the time they are applied. At Mt. Morgan, Queensland, a solution of chlorine in water was similarly used, 100-ton charges of ore being leached in rectangular concrete vats, 60 by 12 by 5 ft, lined with pitch, and provided with bottom filters of sand resting on perforated planks and joists. This was superseded by the permanganate-chlorine process.

The *Black-Elard*, or permanganate, process employs long contact with a solution of potassium permanganate, salt, and sulphuric acid (about 6 lb, 120 lb, and 140 lb to 5 tons or 1,000 imp gal of water) the color indicating its strength. The original Etard formula used permanganate and hydrochloric acid.

The *Mears* process is barrel chlorination in which gaseous chlorine is pumped into the charge under its own pressure. This first employed bleaching powder and acid to produce the pressure. Newbery and Vautin used air pressure to accelerate the action of the chlorine, and the Pollok patents specify water pressure. Ankeny used the more expensive bromine in place of, or in conjunction with, chlorine. Many other early patents dealing with chlorine and bromine are described in O'Driscoll's "Notes on the Treatment of Gold Ores."

In California, precipitation was usually effected by ferrous sulphate, made by the action of sulphuric acid on scrap iron. Sulphur dioxide was commonly used in conjunction with the Colorado barrel process, generated in iron retorts from sulphuric acid and sulphur or charcoal, or hydrogen sulphide, and sawdust filters. Charcoal was used as precipitant at Mt. Morgan. The solutions were usually passed through boxes filled with scrap iron to precipitate copper or silver before being discharged.

Roasting was usually effected in California by hand-rabblled, wood-fired reverberatories; elsewhere in White-Howell or Bruckner cylinders, Pierce turret furnaces, Merton or Edwards furnaces, etc. At Mt. Morgan the Richards furnace was used,

cascading the ore from successive shelves. Residues from pyritic ores were often ground for paint.

The **Patera process** utilizes the solubility of silver chloride in solution of sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , the hyposulphite of photography) and precipitation of silver as  $\text{Ag}_2\text{S}$  by  $\text{Na}_2\text{S}$ . This was suggested by Percy and first applied by von Patera at Joachimsthal in 1858.

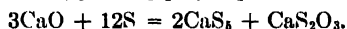
The ore is roasted with addition of salt (4 to 8 per cent), part added near the finish; the hot ore is wetted and allowed to stand some hours to favor chloridizing of the silver. It is then leached in wood vats with warm water to remove base-metal chlorides which also dissolve a little  $\text{AgCl}$ . Hyposulphite solution is then applied and finally wash water, and the effluent run to "base metal" tanks until a trace of hypo is found, then to the silver tanks. The base solution may be precipitated by  $\text{Na}_2\text{S}$ , or  $\text{Ag}$  may be thrown down by cement copper, and copper by scrap iron, or iron may be used at once. The silver solution is precipitated by sodium sulphide, carefully avoiding an excess; after separating  $\text{Ag}_2\text{S}$  by settling or filtration the solution can be used again.

A suitable solvent is 0.5 per cent of crystallized  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , but up to 2 per cent may be used in absence of base metals; 1 ton of 0.5 per cent solution dissolves 30 to 40 oz. of silver. It also dissolves  $\text{PbSO}_4$  and  $\text{PbCl}_2$ ; adding  $\text{Na}_2\text{CO}_3$  then precipitates  $\text{PbCO}_3$ . Sulphates retard solution of silver, free alkali is more prejudicial.

Commercial sodium monosulphide may be used as precipitant, or a polysulphide ( $\text{Na}_2\text{S}_4$  or  $\text{Na}_2\text{S}_6$ ) may be made by heating caustic soda with sulphur (see under Kiss Process).

The vats used were generally small, occasionally up to 25 or 50 tons capacity. The precipitated sulphide was usually filtered in conical canvas bags hung on iron rings in a frame; a filter press was sometimes used. The dried precipitate was sometimes refined by charging upon fused lead on a cupel, or might be smelted with lead ores.

The **Kiss process** nominally substitutes calcium thiosulphate and sulphide for the sodium salts used by von Patera. The precipitant is usually made by boiling lime and sulphur by means of steam, yielding polysulphide and thiosulphate:



The precipitated  $\text{Ag}_2\text{S}$  is therefore mixed with excess sulphur and thiosulphate added to the solution. Starting originally with  $\text{Na}_2\text{S}_2\text{O}_3$  this would gradually be replaced by the calcium salt, but part of the calcium is usually precipitated by sulphates as  $\text{CaSO}_4$  and additional sodium is introduced from salt in the charges. About 3 lb. of lime and 2 lb. of sulphur with a ton of water would make enough precipitant for 50 to 100 lb. of silver.

O. Hofmann states that, with ores containing little or no Cu, the per cent of silver chloridized may be increased by using  $\text{CuCl}_2$  (or a mixture of 3 to 4 lb. bluestone and 6 to 8 lb. salt per ton of ore), added by degrees to the preliminary wash water.

In the **Russell process**, it is claimed that a treatment with "extra solution" containing some  $\text{Cu}_2\text{S}_2\text{O}_3$  (prepared by adding bluestone to thiosulphate) extracted additional silver and was much more effective in dissolving gold.

The **Augustin process** consisted in giving a chloridizing roast to silver ore or matte, and leaching with a strong solution of common salt which dissolves silver chloride to a limited extent. The silver was then precipitated by metallic copper, and the copper by scrap iron. The cement copper was then melted and granulated for reuse.

The **Ziervogel Process**.—Argentiferous matte was roasted to form sulphates, cautiously raising the temperature to decompose those of iron, copper, etc., while

silver sulphate remained unchanged, and was leached out by hot water. The process was also applicable to ore

Silver sulphate (Hofman and Wanjukoff) begins to decompose at  $917^{\circ}\text{C}$ . and is completely reduced to metal at  $923^{\circ}$ , copper sulphate, stable up to  $653^{\circ}$  is completely converted into  $\text{CuO}$  at  $736^{\circ}$ , zinc sulphate at  $767^{\circ}$ , ferrous sulphate passes into basic ferric sulphate between  $167^{\circ}$  and  $480^{\circ}$ , while ferric sulphate begins to dissociate at  $492^{\circ}$  and is completely converted into  $\text{Fe}_2\text{O}_3$  at  $560^{\circ}\text{C}$ .  $\text{Ag}_2\text{SO}_4$  dissolves in 180 parts of cold or 90 of hot water, and is much more soluble in hot, dilute sulphuric acid, in either case it is precipitable by copper, iron, or sulphides

In the *Claudet process*, the product of a chloridizing roast of copper pyrites was leached with solution of sodium and ferric chlorides, which dissolved  $\text{AgCl}$ ,  $\text{CuCl}_2$ , and some  $\text{PbCl}_2$ . By addition of  $\text{ZnI}_2$  (or  $\text{NaI}$ ) silver was thrown down quantitatively as  $\text{AgI}$ , together with some  $\text{CuI}$  and  $\text{PbI}_2$  and any gold which may have dissolved. The precipitate was separated, washed, and reduced with metallic zinc, yielding spongy silver and a solution of  $\text{ZnI}_2$ , which was used again as precipitant

Or, by digesting the precipitate of  $\text{AgI}$ , etc., with sodium sulphide,  $\text{Ag}_2\text{S}$  was formed and  $\text{NaI}$  regenerated as a precipitant

*Gibbs' process* was similar, but employed  $\text{H}_2\text{S}$  gas as a precipitant, until about 5 per cent of the  $\text{Cu}$  was precipitated, which insured all the silver being thrown down

### SILVER AMALGAMATION

The **Patio process** was originated by Bartolomé de Medina about 1557, for the rich silver ores of Pachuca, and was widely used in Mexico and in South American countries. This process is described at length in Chapter XXXIII, "Chlorine in Metallurgy."

The *Patio process* was worked for some time in Nevada on Comstock ore, but failed owing to climatic conditions, and thus led to the adoption of the Washoe or pan-amalgamation process

The **Washoe process**, or pan amalgamation, was developed at the Comstock mines, Washoe County, Nevada, the ore being stamped dry or wet, and the pulp treated in batches, usually three per pan daily. The pans differed greatly in detail, having cast-iron bottoms with wood staves or sheet-iron sides, and a central cast cone through which ran a vertical shaft carrying a muller with cast segmental shoes, similar cast-iron dies were attached to the bottom. Means for raising and lowering the muller were provided by threaded handwheels forming lock nuts at the top of the shaft, or by carrying the step bearing of the shaft on an adjustable lever. Three curved iron wings were usually fastened to the sides or hung from the wooden cover. A steam chamber was often provided under the pan bottom

The charge was usually 1,500 to 3,000 lb., but might range from 800 to 5,000. A batch of pulp was run in, after thickening in a wooden tank if wet crushed, the muller was lowered and the charge ground 1 to 3 hr., steam being admitted to the false bottom, or run directly into the pulp by a hose. Mercury was then added, at least 10 per cent the weight of the dry pulp (often 300 or 350 lb. altogether), the muller raised clear of the dies and run 3 or 4 hr. Chemicals were generally added with the mercury, usually copper sulphate and salt, sometimes sulphuric acid or metallic iron, though the iron was often derived from the wear of the pan castings

The pulp was then thinned with water and run to a shallow separator or settler with vertical shaft carrying four arms with iron or wooden ploughs. Here the

bulk of amalgam and mercury separated and were drawn off at a siphon tap. In some cases this stage was carried out in the grinding pan, revolving the muller slowly.

The pulp then ran to an agitator—a deeper pan with wood sides, with four revolving arms carrying vertical slats, to settle a little additional amalgam and coarse material, and was finally drawn off running to waste or to a settling dam. All settlers etc., were provided with holes in the sides closed by wood plugs for discharging pulp. At the Comstock, 70 to 85 per cent is said to have been extracted from the sulphide ore, but at custom mills the usual return was only 65 per cent of the assay value of samples taken at the mortar lip.

*Barrel amalgamation* (Freiberg process) was carried out in stout, wooden barrels rotating on a horizontal axis. The ore was roasted with salt, and charged in the barrel with water and scrap iron, which dissolved silver chloride and reduced it to metal, cupric and ferric salts being also reduced to cuprous and ferrous; mercury was then added and rotation continued 16 to 20 hr., more water was then added to thin the pulp, and after a short period of rotation the mercury was drawn off and the ore washed out by a stream of water. This process was used for some time on the Comstock lode.

*The Cazo process* or hot pan amalgamation was devised by Alonzo Barba in Peru about 1609 for rich oxidized silver ore. The *cazo* or pan first used was a small copper pan; the later *fondon* had a copper bottom about 6 ft. in diameter and 6 to 8 in. thick, to which wood staves were fitted. Two large copper mullers were made to revolve around it, and a fire was maintained under the bottom. See pp. 1092 and 1152 for a complete description.

*The Boss continuous process* was an attempt to make the Washoe pan-amalgamation process continuous, by using a series of steam-jacketed pans set on a slight grade so that pulp flowed from one to the other and finally through settlers; the mercury similarly flowed through a pipe system to a safe (as was done at some of the Washoe plants) where it passed through a conical canvas filter to separate solid amalgam, the filtered mercury being pumped back to the topmost pan.

*The Reese River process*, applied by Stetefeldt to the very base sulpharsenical ores of central Nevada, involved a chloridizing roast of the ore, wetting and cooling it on a floor, followed by a pan treatment similar to the Washoe process. A very impure bullion resulted. A similar system was used in Butte and elsewhere in Montana.

*The Combination process*, adopted by the Montana Co. about 1890, consisted in concentrating the gold-silver ore coming from the stamp mill before thickening the tailing and treating it by the pan process. A great economy in mercury was effected by thus removing arsenical copper minerals. The original equipment was fifty stamps with amalgamating plates, twenty frues, twenty-four pans, twelve settlers, five agitators, and finally twenty frues for the pan tailing, which was then impounded.

*The Kroehnke process* consisted in treating crushed ore in rotating wooden barrels of the Freiberg type, with mercury and a strong solution of cuprous chloride in brine, and then adding zinc amalgam; lead amalgam was used with poorer ore. The impure coppery amalgam was then purified by treatment with hot brine and bluestone acidified with sulphuric acid, and finally centrifuged and retorted. The process is thoroughly described by Schnäbel.

**Conversion Tables for Assay Valuations.**<sup>1</sup>—In English-speaking countries the weights of precious metals are usually expressed in Troy ounces (of 480 gr.) and fractions of ounces are stated in decimals, the troy pound, pennyweight, etc. being but little used. Other nations generally use the metric system for these as for other metals, and this system is adopted in many United States statistical

<sup>1</sup> Revised, 1924, from the author's paper in "*Mines and Minerals*," January, 1909.

reports. The purity or "fineness" of these metals is expressed either in carats (twenty-fourths) or in parts per thousand (millièmes), pure gold being designated as 24 k. or 1,000 fine.

**Gold.**—The exact value of 1 troy oz. of pure gold is \$20.671834625323+, corresponding to the coinage of \$8,000 from 387 oz. of fine gold, or 430 oz. of gold 900 fine—the United States standard since 1834. Standard British coinage gold is 22 k. or 916.666 fine, and 480 oz. of standard gold, or 440 oz. of fine gold, coin exactly £1,869. Hence 1 oz. of fine gold is worth 1,019.454545 d. For ordinary metallurgical calculations, the values assumed for an ounce of fine gold are \$20.67 and 1,020 d. (85 s. or £4.25 sterling), and these approximate figures are used in these tables. The United States values used are, therefore, about 1 in 10,000 too low, and the British about 1 in 2,000 too high. At the values adopted the dollar is equivalent to 4.11224 s. and the pound sterling to \$4.86353. (This must not be confounded with the pound of the post-war exchange which was not on a strictly gold basis). The United States Mints report gold bullion assays to the nearest  $\frac{1}{4}$  per 1,000; the London Mint to  $\frac{1}{10}$  per 1,000. In statistical work the United States Mint uses the exact figure first given, making a kilogram of pure gold worth \$664 60, and a gram 66.46 cts.

**Silver.**—In the United States the price of silver is stated in cents per troy ounce of metal nominally 1,000 fine. London quotations are pence per troy ounce of "sterling silver" 925 fine, which, except for short periods, was the standard for British silver coin from 1066 to 1920. Since 1920, British silver coins have been reduced to a fineness of 500.

1 penny per ounce 925 fine = 2.19 cts. per fine ounce.

1 cent per fine ounce = 0.457 pence per ounce 925 fine.

United States silver coin is 900 fine, 110 standard oz. or 99 fine oz., coining \$128; the Mints report the fineness of silver bullion to the nearest one-half part per 1,000.

The following foreign or obsolete units sometimes occur in reports: S. America: 1 marco per cajon varies between 100 and 70 parts per million, or grams per metric ton. Russia: 1 dola ( $\frac{1}{16}$  zolotnik) per 100 poods = 2.71 parts per million, or 1.63 cents gold per ton. Mexico 1 adarme ( $\frac{1}{16}$  onza) = about \$1.20 gold. Old German. 4 quentchen = 16 denaer = 1 loth.

FINENESS OF BULLION AND ALLOYS OF PRECIOUS METALS

Denomination	Equivalent in millièmes or parts per 1,000	
1 k . . .	41 666	{ 24 k. = 1 lb. trov (England) 24 k. = 1 mark (Germany, etc.)
1 grain per marc	0 217	4,608 gr. = 1 marc of 8 oz. (France, Spain, etc.)
1 oz. per marc	125 000	8 oz. = 1 marc (France, Spain, etc.)
1 loth (silver)	62 500	16 loth = 1 mark (Germany, etc.)



## ASSAY VALUATIONS

Values	One part in	Per cent	Per metric ton			Per long ton of 2,240 pounds			Per short ton of 2,000 pounds		
			Troy ounces	U S dollar-gold	Grams	Troy ounces	U S dollar-gold	Troy ounces	Troy ounces	U S dollar-gold	Troy ounces
1 per cent	100	1	321 50	6 645 406	10 000	328 666	6 752 20	291 666	6 028 75		
1 g per metric ton = 1 part per million	1 000 000	0 0001	0 03215	0 6645	1	0 03266	0 675	0 029166	0 6029		
1 pennyweight	29 166 66	0 0032857*	1 1023	22 7845	34 2857	1 120	23 15	1	20 67		
1 troy oz per short ton	32 666 66	0 0030612†	0 9842	20 3434	30 612	1	20 67	0 892857	18 458		
1 troy oz per long ton	32 150	0 0031104‡	1	20 67	31 104	1 016	21 00	0 90720	18 752		
1 troy oz per metric ton	602 875	0 0016587	0 053285	1 1023	1 6587	0 054155	1 12	0 048379	1 57		
1 gold per short ton	384 000	0 0002604	0 083724	1 73**	2 604	0 08507	1 758	0 075054	1 57		
One solotnik per 100 pounds	3 200	0 03125	10 0468	207 66	312 5	10 2183	211 21	9 11458	188 14		
One loth per centner	16 384	0 00610	1 9623	40 56	61	1 9938	41 2118	1 78654	36 80		
One octavo per quintal											

\* = 24 † = 3680 ‡ = 2443  
 \* = 7 000

## CONVERSION TABLES—WEIGHTS

	Grains	Penny weights	Troy ounces	Avoirdupois ounces	Avoirdupois pounds	Grams	Fine Gold value	
							United States	British
1 grain	1	0 041666	0 0020533	0 00228571	0 000142857	0 0648	4 306 cts	2 125d
1 pennyweight	42	1	0 0500	0 0548571	0 00342857	1 5552	\$1 0335	4 25s
1 troy oz	480	20	1	1 0971428	0 0685714	31 104	\$20 67	85s
1 avoirdupois oz	437 50	18 22917	0 911458	1	0 06250	28 35	\$18 84	77 474s
1 avoirdupois lb	7 000	291 666	14 58333	16	1	453 60	\$301 4375	£61 97
1 mg	0 015432	0 000643	0 00003215	0 000035274	0 0000022046	0 0010	0 06645 ct	0 033 d
1 gram	15 432	0 643	0 03215	0 035274	0 0022046	1	66 45 cts	2 73275s.
1 kg	15 432	643	32 15	35 274	2 2046	1 000	\$664 54	£136 04

VOLUME AND WEIGHT OF FINE GOLD AND SILVER

	1 c c	1 cu in	1 cu ft
Fine silver			
Weight grams	10 57	173 21	299 307
Weight troy ounces	0 339825	5 5687	9,622 72
Fine gold			
Weight grams	19 3	316 269	546,513
Weight troy ounces	0 6205	10 1680	17,570 39
Value U S dollars	\$12 8257	\$210 17	\$363,180
Value pounds sterling	£2 647	£43 214	£74,674

TABLE 1 -PULP FORMULAS

$d$  = density or specific gravity of dry solid (ore, sand, or slime)

$p$  = specific gravity of pulp (mixture of water and ore, etc.)

$S$  = percentage by weight of dry solid in pulp

= grams in 100 grams, tons in 100 tons weight, etc

$R$  = water ratio or dilution of pulp

= tons water per ton of dry solid

= grams water per gram of solid

$V$  = volume percentage of solid in pulp

= cubic centimeters in 100 c c pulp.

= cubic feet in 100 cu ft pulp

$F$  = solid factor

= grams solid in 100 c c of pulp

= tons solid in 100 fluid tons or 3,200 cu ft of pulp

= avoirdupois ounces in 0.1 cu ft of pulp

$k$  is a constant for any particular solid under consideration, used to facilitate calculation, and depending upon the density of the dry solid

$$k = \frac{100d}{d-1}$$

$$d = \frac{p}{1 - R(p-1)} = \frac{Sp}{100(p-1)}$$

$$p = \frac{R+1}{R + \frac{1}{d}} = \frac{100}{S(d-1) - k - S}$$

$$S = \frac{100}{R+1} = \frac{100d(p-1)}{p(d-1)} = \frac{k(p-1)}{p}$$

$$R = \frac{d-p}{d(p-1)} = \frac{1 - \frac{p}{d}}{p-1} = \frac{100-S}{S}$$

$$= \frac{100}{S} - 1 = \frac{100p}{k(p-1)} - 1$$

$$F = Sp = \frac{100p}{R+1} = \frac{100d(p-1)}{d-1} = k(p-1)$$

$$V = \frac{F}{d} = \frac{Sp}{d} = \frac{100(p-1)}{d-1} = (k-100)(p-1)$$

$$\text{Volume percentage of water in pulp} = 100 - V = 100 - \frac{F}{d} = p(100 - S)$$

$$= \frac{100(d-p)}{d-1}$$

$$\text{Tons of dry solid per 100 tons water} = \frac{100}{R} = \frac{100S}{100-S} = \frac{100d(p-1)}{d-p}$$

$$\text{Fluid tons pulp to yield one ton solid} = \frac{100}{F} = \frac{100}{k(p-1)} = \frac{R+1}{p}$$

WATER AND SOLIDS IN PULP

	Weight pulp	Volume pulp	Weight dry solid	Weight water	Volume water
1 ton of pulp (2 000 lb)	1 ton	$\frac{1}{p}$ fluid ton $\frac{32}{p}$ cu ft	$\frac{S}{100}$ ton $\frac{R+1}{(p-1)k}$ ton $\frac{100p}{(p-1)k}$ ton	$\frac{d-p}{p(d-1)}$ ton	$\frac{d-p}{p(d-1)}$ fluid ton $\frac{32(d-p)}{p(d-1)}$ cu ft
1 fluid ton of pulp (32 cu. ft., 240 U S gal, 200 imp gal)	$p$ tons	1 fluid ton 32 cu ft	$\frac{(p-1)k}{100}$ ton	$\frac{d-p}{d-1}$ ton	$\frac{d-p}{d-1}$ fluid ton $\frac{32(d-p)}{d-1}$ cu ft
1 cu ft of pulp (7.5 U S gal, 6.25 imp gal)	62.5 $p$ lb	1 cu ft 0.03125 fluid ton	$0.625(p-1)k$ lb $\frac{(p-1)k}{3200}$ ton	$\frac{62.5(d-p)}{d-1}$ lb $\frac{d-p}{32(d-1)}$ ton	$\frac{d-p}{d-1}$ cu ft
1 ton of dry solid (2,000 lb)	$R+1$ tons $\frac{100p}{(p-1)k}$ ton	$\frac{100}{(p-1)k}$ fluid ton $\frac{3200}{(p-1)k}$ cu ft	1 ton	$\frac{R}{S} \frac{(100-1)}{(d-p)}$ ton $\frac{d(p-1)}{d(p-1)}$ ton	32 $R$ cu ft $R$ fluid tons
1 fluid ton of water (32 cu ft., 240 U S gal, 200 imp gal)	$\frac{p(d-1)}{d-p}$ ton	$\frac{d-1}{d-p}$ fluid ton	$\frac{1}{100} \frac{R}{S} \frac{d(p-1)}{d-p}$ ton $\frac{100-S}{100-S}$ ton	1 ton	1 fluid ton 32 cu ft

1 U S gal of pulp =  $\frac{(p-1)k}{12}$  lb dry solid 1 imp gal of pulp =  $\frac{(p-1)k}{10}$  lb dry solid

Metric Values.—The relation between the metric ton (of 1 000 kg) and the cubic meter (1 000 liters) is identical with that existing between the ton of 2,000 lb and the fluid ton of 32 cu ft. For instance 1 cu m. of pulp contains 0.01  $(p-1)k$  metric ton dry solid

$k$  is a constant for any value of  $d$   $k = \frac{100d}{d-1}$

$d = 2.5$   
 $k = 166.7$  162.5 158.8 155.5 152.6 150

2.6 2.7 2.8 2.9 3.0

These formulas are strictly applicable only to mixtures of solids with liquids of specific gravity 1.00, such as water or cyanide solutions at ordinary temperatures.

**Measurements of Daily Tonnage.**—Several accurate methods are available; one depends on the direct weighing of the dried material caught during a measured interval of time; another on the measurement of time and the corresponding volume of pulp, together with the specific gravity of the pulp, using the known relations between the gravity and solid contents of pulp. Or one may estimate the flow of pulp by a weir or any other method and then determine the weight of solid in a measured volume. Reduced to the simplest terms the computations from such data may be made by one or the other of the following formulas,

$$\text{Tons solid per day} = \frac{\text{pounds dry solid caught} \times 43.2}{\text{seconds observed}} = 43.2 \times \text{pounds per second}$$

$$\text{Tons solid per day} = \frac{2,700d}{d-1} \times \frac{p-1}{t}$$

This formula may be arranged for slide-rule calculation

where  $t$  = seconds required to yield 1 cu. ft. pulp.

$p$  = specific gravity of pulp.

$d$  = specific gravity of dry solid.

$k$  = a constant for any particular material.

$$\text{Tons solid per day} = \frac{(27k)(p-1)}{t}$$

$$\begin{array}{ccccccc} d = & 2.5 & 2.6 & 2.7 & 2.8 & 2.9 & 3.0 \\ 27k = & 4,500 & 4,390 & 4,290 & 4,200 & 4,120 & 4,050 \end{array}$$

$p$  may be obtained by a hydrometer in the case of slime pulp, or by weighing in grams the contents of a glass or tin liter flask, or by weighing in pounds the content of a bucket graduated to hold 100 lb. of water. (Such a bucket may be 14 in. in diameter, and 20 in. deep, in which case the graduation for 100 lb. is about 18 in. from the bottom.) 100 lb. water = 1.6 cu. ft. The value of  $t$  may be observed with a stop watch filling a 100-lb. bucket, but preferably with a much larger container.

$$\text{Tons solid per day} = \frac{\text{cubic feet per day} \times \text{pounds per cubic foot}}{2,000}$$

## CHAPTER XXX

### HYDROMETALLURGY OF COPPER

By H. A. TOBELMANN<sup>1</sup>

**Leaching** is the term applied to the process of recovering a metal from an ore by a solvent or lixiviant and the removal of the resulting solution from the undissolved portion. In other words, leaching is the recovery of a metal from ore by a wet process.

In general, leaching is applied only to ores which are not adapted to treatment at an equal or greater profit by the longer established methods, such as gravity concentration, flotation, or smelting. It has not yet been applied on a large scale to copper ores containing a considerable quantity of precious metals, as the recovery of these is not high with the usual copper lixiviants. Its most extensive application so far has been in the treatment of low-grade oxidized ore, in which the copper is largely soluble in dilute sulphuric acid. It has been estimated that between 10 and 15 per cent of the copper output of the world is produced by leaching. In this connection, it is of interest to note that the two largest leaching plants in operation at the present time produce copper at a cost so low that it is not equalled by any other method of treatment.

The oxidized copper minerals, such as the carbonates and silicates, are readily attacked by a number of the more common acids and alkalis while the non-oxidized or sulphide minerals are not and must first be prepared by roasting, weathering, or other means of oxidation, either with or without added chemical agents.

The leaching of copper ores can be carried out in the following ways: leaching in place; heap leaching; and confined leaching.

**Leaching in Place.**<sup>2</sup>—This method is based upon the fact that when an orebody containing sulphide is broken up so that both air and water have access to the ore, the sulphide portion of the mineral is decomposed and soluble sulphates are formed. The chemical reactions involved in this transformation of sulphides into oxidized forms have been discussed by Lindgren.<sup>1</sup> The behavior of sulphides of the same kind may be very different, oxidation sometimes not taking place for a long period and then again taking place so rapidly as to show decomposition within a few weeks. The more porous and more absorbent the gangue, the more rapidly will the ore respond to treatment. This method, which consists of treating ore without removing it from the mine, has been applied only to exhausted orebodies and to mines containing large quantities of ore of such low copper content as to make its removal unprofitable, and in such a broken-up condition as to be provided with ample crevices for the circulation of both air and solution.

The action is very slow, but the method is inexpensive, the principal operating cost being the pumping and distribution of the solution and the iron and precipitation

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<sup>2</sup> References in this chapter are to similarly numbered references in the Bibliography at the close of the chapter.

expense. The efficiency of the process in any particular case cannot be determined, as there is no known method of accurately determining the tonnage and copper contents either before or after operations

The leaching results are obtained by the intermittent circulation of water and air through the crevices in the ore. One of the greatest difficulties of the process is that the slimes gathered from the ore and the accumulated salts may in time fill these crevices and temporarily, if not permanently, protect the exposed ore from further leaching action. Usually, the rate of extraction is quite rapid at first, but it decreases continually. The solutions from such an operation are nearly always impure and the precipitation of the copper by scrap iron would be the only method that could be considered

Leaching in place is neither new nor novel and is recorded to have been successfully used on a small scale in Hungary during the fifteenth century. J. Paike Channing<sup>1</sup> states that copper was extracted by this process from the Eureka mine in the Ducktown district as early as 1850. According to Philip Argall,<sup>2</sup> the Cronebane mine in Wicklow County, Ireland, was a good example of the application of this method. In this case numerous small drifts were driven immediately under the gossan and water was introduced into the loose gossan on the surface. The solution, after being directed from one level to another through stopes and fillings, was pumped from the lowest level to the surface, where the copper was precipitated. Irving<sup>4</sup> refers to a similar operation at the Aznalcollar mines in Spain. It has also been applied to some of the exhausted mines at the Rio Tinto.<sup>5</sup> The simplicity and the effectiveness of this method remained apparently unnoticed in the United States until the spring of 1923, when the Ohio Copper Co. of Utah<sup>6</sup> began the leaching of a large body, estimated to contain about 38,000,000 tons at 0.3 per cent copper, of thoroughly broken copper-bearing quartzite. The shattered quartzite itself is practically inert to chemical action, while the copper minerals existing principally in the fissures of this material are readily attacked by the leach solutions. Thus, there is little danger of clogging the ore body by decomposition or alteration products, as is so apt to occur in monzonite-porphry ore bodies.

The present operation consists of carefully distributing on top of the caved ore area 1,200 to 1,500 gal. per minute of solution consisting of about two-thirds fresh water and one-third launder tailings solution. The solution going on the ore will average about 0.3 to 0.4 lb. of copper and 8 to 10 lb. of iron per thousand gallons. This solution percolates through the caved ore and is collected at the bottom of the shaft, where it is directed to the precipitation launders, situated on both sides of a large haulage tunnel. The solution entering the launders will average about 15 to 20 lb. of copper and from 2 to 3 lb. of iron per thousand gallons. There are two parallel launders, 32 in. by 32 in. by 1,600 ft. long, in which 97 to 98 per cent of this copper is precipitated. Additional launders outside of the haulage tunnel are provided to precipitate any remaining copper.

It will be noticed that iron is precipitated out of solution during its passage through the ore. This may be due to hydrolysis or to the action of the ferric sulphate on the oxidized copper minerals in the ore, or both. Should this precipitation at any time seriously interfere with the percolation of solution, the further caving of a small quantity of ore, or acidulation of the water, would probably relieve this condition. It is of interest that solutions both going on and coming off the ore are practically neutral. Clean scrap is used and, due to the intelligent operation and supervision, an unusually high-grade precipitate is the result. The average precipitate produced by this company up to the present time will analyze over 90 per cent copper, the impurities being those due to the entrained solution and consisting principally of iron and aluminum sulphates. The cement copper usually produced from such operations will average not over 70 per cent copper. The production of such a plant is necessarily

largely dependent upon the fresh water available. With the present pumping capacity, the Ohio Copper Co. is consistently producing some 700,000 to 900,000 lb. of copper per month, or approximately 30,000 lb. per day. The total cost of operation has been published<sup>7</sup> as being 6 to 6½ cts. per pound, f o b New York, a cost which is rarely equaled. Of this amount, it is said that 50 per cent represents the pumping and precipitation costs.

The success which has attended the operations of the Ohio Copper Co. will result in great attention being paid to this ridiculously simple yet highly profitable process. There are, no doubt, many worked-out ore bodies sufficiently broken up and of such mineralogical composition as to make this method applicable.

Precipitation should be carried on underground when conditions make it practical. The warmer the solutions the more efficient both the leaching and the precipitation will be. Also, it is more difficult to pump solutions containing copper sulphate than those containing iron sulphate. Efficient precipitation cannot be accomplished with heavy scrap iron like car wheels, slag pots, and old rails, yet this is the practice generally tried, resulting in condemning the precipitation of copper by iron in general.

**Heap Leaching.**—This method of leaching is probably one of the oldest, if not the oldest, of the methods for the recovery of copper from ores. It is said to have been used as early in 1752<sup>8</sup> in recovering the copper from cuperiferous pyrite in Spain. This method, like the one first described, depends upon the natural oxidation of the sulphide minerals by continual subjection to air and water. The chemistry of this oxidation has been much discussed, but still it is not accurately known.

Ores, both sulphide and mixed ore, which must be removed from the mine but which are too low grade to treat at a profit by any other method, can be treated by heap leaching. This is generally carried on as follows:

Ground with a slight slope is selected. It is cleared of any growths, and is then rolled and packed with clay or slimes to make it as near waterproof as possible. Large boulders of ore are selected for building culverts and cross-culverts for drainage and ventilation purposes, and the drainage is directed to a common point. The ore, without crushing or other preparation, is now carefully piled on this prepared area. In some cases, it has been found helpful to classify the material to the extent of placing the coarsest material on the bottom and the finest on the top as an aid to both the ventilation and the solution circulation. The top of the ore piles is provided with distributing trenches. Solution, consisting at first of fresh water and later of waste solution from which the copper has been precipitated, is directed over the ore pile. The wetting is so conducted that, while a certain section is being saturated with solution, other sections are permitted to heat and oxidize. In each passage of the solution through the ore, the sulphates that have formed from the oxidation of the sulphides are dissolved and washed away. The solution emerging from the bottom of the pile is directed to a sump, from which it is pumped to scrap-iron precipitation launders, where the copper is recovered as cement copper. The solution with the copper removed is pumped back to the ore for further leaching.

The method is quite simple, but the reaction is very slow. As years are required to obtain a commercial extraction, this method can be profitably applied only to very large tonnages. The principal method of recovering copper at Rio Tinto has been by a heap-leaching process. Two classes of ore are leached by this method, a pyrite and a quartz. When leaching sulphides, the fines and the coarse are treated together. The heaps are from 10 to 40 ft. high. The tops are divided into squares for better solution distribution. According to De Kalb,<sup>6</sup> there are said to be some 20,000,000 tons, occupying about 350 acres, undergoing treatment. The heaps have been placed

on a gently sloping hillside having a naturally impervious floor. About 150 gal. of solution per ton of ore per year are required. About 60 per cent extraction is generally made in the first three years, while seven to nine years are required to bring this up to 80 or 85 per cent. It is also said that some of these piles have been under treatment for nearly thirty years. The pyrite itself is barely attacked and is sold for its sulphur value.

A series of small-scale heap-leaching tests made by the Phelps-Dodge Corporation at Bisbee, Ariz., on the low-grade ores of Sacramento Hill were so encouraging that it was decided to use this method to treat some 8,500,000 tons of similar ore which will be available. According to Hudson and Van Arsdale,<sup>9</sup> about 400,000 tons per year will be available for heap leaching. Preliminary tests indicate that about six years will be required to make a total recovery of 70 per cent, divided as follows:

	PER CENT
First	20
Second	12
Third	10
Fourth	10
Fifth	9
Sixth	9

This is probably the first real application of heap leaching to ores in this country, and the beginning of the extensive use of a method which not only is one of the cheapest, but also one of the oldest known. The installation expense is low, not much labor is required, and the final product is high grade. On the other hand, the reaction is in all cases very slow and may even cease by the gradual filling up of the crevices upon which the reaction depends, by slimes and basic non-salts. Under certain conditions, iron is precipitated out of solution and forms an insoluble coating on the material on which it is deposited. Such a condition might possibly protect the exposed copper surface from any further leaching action.

Heap roasting followed by subsequent heap leaching has been practiced. Schnabel speaks of a process at Rio Tinto which consisted of slowly roasting elliptical heaps of sulphides containing some 1,500 tons of ore. After roasting, the pile was leached with water, whereupon the larger portion of the copper was recovered. The partially leached ore was now restacked over horizontal flues to permit of thorough ventilation and was moistened from time to time, whereby much of the remaining copper was recovered. The copper was precipitated by iron.

**Confined Leaching.**—By confined leaching, the leaching of an ore in tanks or vats is meant. This may be accomplished in two ways, either by agitation or by solution circulation, depending largely upon whether the ore must be finely ground or not to give a profitable extraction. This form of leaching may be divided into the following principal operations: (1) reduction to size, meaning the necessary crushing, grinding, and screening, (2) the converting of the copper mineral to an oxide or sulphate by roasting or otherwise, if it exists in a non-oxidized form; (3) dissolving the copper in the cheapest and most suitable reagent and removing the resultant solution from the undissolved portion of the ore, (4) washing the treated ore so as to recover the entrained copper solution, (5) the precipitation or removal of the copper from these pregnant solutions.

**Reduction to Size.**—The fineness to which an ore will have to be crushed to give a commercial extraction is largely dependent upon its porosity, the size of the mineral grain, the degree of dissemination, and the rapidity with which the mineral is attacked by the lixiviant used.



In most cases where copper ores are treated by leaching, the mineral exists as seams or filling of fissures and fine grinding is resorted to only when rapid extraction is desirable or necessary. Rarely, however, is the copper-bearing mineral so disseminated and so surrounded by an impervious gangue that fine grinding is necessary for releasing the mineral particles in order to give access to the solvent. The typical material leached at Chuquicamata is an example of the copper mineral occurring in seams and the filling of fissures, whereas the material treated at Ajo would be an example of the more distributed copper minerals.

The influence of screen size on extraction can be seen from the accompanying table. This table shows the mesh, the per cent of copper in heads and in tailings, and the extraction on material of the different mesh for the year 1920 at the New Cornelia Copper Co.'s plant at Ajo, Ariz.<sup>10</sup> During this year sizing tests were made of each head and tailing sample, composited monthly and analyzed. The average for the year was then computed.

DISTRIBUTION OF TOTAL OXIDE, SULPHIDE, AND SOLUBLE COPPER IN THE HEADS AND TAILINGS FOR DIFFERENT MESH HEADS, PER CENT COPPER

Mesh	Per cent	Total	Oxide	Sulphide (by difference)	Soluble	Insoluble (by difference)
On 3	26.6	1.37	1.23	0.14	1.24	0.09
On 4	18.6	1.33	1.18	0.1	1.23	0.10
On 6	13.2	1.39	1.25	0.14	1.30	0.09
On 8	9.1	1.16	1.30	0.16	1.34	0.12
On 10	6.4	1.05	1.39	0.16	1.43	0.12
On 14	5.0	1.62	1.46	0.16	1.49	0.13
On 20	3.1	1.75	1.77	0.18	1.62	0.13
Through 20	18.0	2.00	1.82	0.21	1.88	0.18
Calculated	100.0	1.34	1.368	0.167	1.416	0.118
Average of assays		1.525	1.362	0.163	1.396	0.125
Composite sample		1.500	1.340	0.160	1.390	0.110

TAILINGS PER CENT COPPER

Mesh	Per cent	Total	Oxide	Sulphide (by difference)	Soluble	Insoluble (by difference)
On 3	25.8	0.47	0.35	0.12	0.37	0.10
On 4	20.1	0.32	0.21	0.10	0.23	0.09
On 6	12.5	0.25	0.14	0.11	0.15	0.10
On 8	8.7	0.21	0.10	0.10	0.11	0.10
On 10	7.2	0.21	0.09	0.12	0.10	0.11
On 14	4.8	0.21	0.11	0.10	0.11	0.10
On 20	3.8	0.22	0.11	0.11	0.12	0.10
Through 20	17.1	0.35	0.19	0.16	0.18	0.17
Calculated		0.328	0.210	0.122	0.223	0.110
Average of assays		0.320	0.202	0.118	0.218	0.102
Composite sample		0.320	0.210	0.110	0.215	0.105

Per Cent Extractions

Mesh	On total copper	On oxide copper	On sulphide copper	On soluble copper
On 3.....	65.69	71.5	14.3	71.1
On 4.....	76.00	82.2	16.5	81.3
On 6.....	82.03	88.8	21.4	88.5
On 8.....	85.62	92.3	31.3	91.8
On 10.....	86.45	92.8	25.0	93.0
On 14.....	87.04	92.4	37.4	92.6
On 20.....	87.43	93.0	38.8	92.6
Through 20.....	83.01	90.2	29.2	90.4
Calculated.....	78.50	84.9	27.0	84.3
Average of assays	78.44			

The coarser the mesh that can be leached the less will be the crushing expenses and the more efficient the circulation. As the time required to leach an ore depends almost entirely upon the solution penetration, it can be seen that the larger the particle of ore the longer the time that will be required to dissolve the copper. The treatment of coarse material entails less expense not only as to crushing, but it is simpler to remove the dissolved copper, there is less copper entrained in the final material discarded, and the less impurities will be dissolved per unit acid neutralized. Coarse grinding will permit of leaching by percolation in tanks in which the material is stationary and the lixiviant moving, so that leaching and removal of the dissolved copper from the gangue is coincident.

In treating coarse material, it is very important to have as much of the material of the same mesh as is practical, as oversize will not be leached and fines will interfere with solution percolation. The necessity of a uniform product for consistent extractions resulted in the adoption of disc crushers<sup>11,12</sup> at Ajo.

As a rule, the richer the material to be leached the finer the grinding necessary for economical extraction. However, the smaller the mesh the greater the quantity of slimes produced and the less efficient will be leaching in tanks. Slimes, when present, cause channeling, which prevents even distribution of solution and interferes with uniform extraction. When fine grinding is resorted to, the material must be classified and the sands and slimes separately treated. Where no classification and separate treatment is feasible, the product must carry the minimum quantity of fines to prevent interference with percolation.

When finely divided material is leached, both the solids and the solution are moving and the separation is accomplished by the standard methods of settling, decanting, and filtering. Probably the coarsest material being treated by a leaching process in tanks and by circulation is at Chuquicamata, where 90 per cent of the material is crushed to pass a 0.371-in. screen. At Ajo about 27 per cent remains on the 0.261-in., or approximately  $\frac{1}{4}$ -in., screen.

The importance of proper and uniform crushing may be seen by the following: If the ore treated by leaching at Ajo had been so crushed that the material remaining on 3 mesh were crushed to pass 3 mesh but not to pass 4 mesh, the extraction would have been increased a little more than 2 per cent, or approximately 0.6 lb. of copper per ton of ore or over 7,000,000 lb. for the 12,000,000 tons thus far leached.

In any form of leaching, whether with an acid or an alkali solvent, slimes must be avoided as much as possible.

**Oxidation or Roasting of Sulphides.**—As has already been stated, copper in an oxidized form is quite soluble, while in the sulphide form it is not. Roasting, which

is essentially oxidation, is resorted to, and ores which are proposed to be treated by a wet process and which consist of all or part sulphides must be roasted.

During roasting, sulphides are not only oxidized or converted to sulphates but under proper conditions a large part of undesirable elements, like arsenic, antimony, and bismuth, can be volatilized. Heat treatment, such as roasting or thorough dehydrating, is an advantage to many ores, making the impurities less soluble, and leaching and filtration less difficult.

To obtain the best results, the proper roasting conditions must be determined for each ore. The literature on the subject is extensive and covers a great many different conditions. It has been found possible under proper conditions so to roast an ore as to convert practically the total copper present in a mixed ore to a water-soluble sulphate.<sup>13</sup>

Roasting is frequently carried on in the presence of, or with the aid of, a reagent, usually sodium chloride, or common salt, with the object of converting the copper into a more soluble chloride and the silver into a more soluble compound. Roasting with sodium chloride, however, requires careful regulation of temperature, since, under certain conditions of temperature and certain ratios of salt and sulphur, the copper may be almost completely volatilized (see Chap. XXXIII, Chlorine in Metallurgy).

**Dissolving the Copper.**—Many lixiviants have been proposed for dissolving the copper in an ore. These include both acid and alkalies and are, in order of their importance, sulphuric acid, ammonia and ammonium carbonate, ferric sulphate, sulphurous acid, ferric chloride, cupric chloride, hydrochloric acid, chlorine, and nitric acid.

Of these, sulphuric acid is the cheapest and the solvent most commonly used. It reacts readily with the oxidized copper minerals, forming copper sulphate. Its action on the copper sulphide minerals is practically negligible. It is, unfortunately, also a ready solvent for many other constituents of ores in which the copper minerals occur—in some cases, to such an extent that it cannot be profitably used. It is always used as a dilute solution, probably never exceeding 10 per cent and seldom exceeding 5 per cent, depending upon the grade of the ore, the time of contact, and the temperature of the lixiviant. Sulphuric acid has a selective action for copper and in very dilute solution will react with copper in preference to the other constituents of the ore.

It has long been recognized that in the leaching of copper ores, as in cyaniding gold ores, the product of the time of contact and the solution concentration is a constant. In other words, if a given ore is leached on a given mesh for 8 days with an average acid concentration of, say, 2.5 per cent, the same extraction will be obtained as when leaching this material sixteen days with half the acid concentration, or 1.3 per cent. The important fact, however, is that in the case of the greater concentration only 50 per cent of the acid was used in dissolving copper, while more than 75 per cent was used when using the lower acid concentration. In other words, the lower the acid concentration the less impurities will be dissolved. In leaching with sulphuric acid, the acid is one of the largest, if not the largest, item of expense, and when electrolysis is used to precipitate the copper, much of the acid combined with elements other than copper is permanently lost. Impurities are objectionable not alone from the point of excessive acid consumption, but also because of their accumulation when the method of precipitation is such that the solution may again be used. Also, impurities may accumulate in a solution to such a point that it will be no longer efficient and it will have to be discarded. The two largest leaching plants in operation at the present time, that of the Chile Copper Co. at Chuquibambilla and that of

the New Cornelia Copper Co at Ajo, Ariz, use dilute sulphuric acid as the leaching agent.

The subject of sulphuric acid leaching processes would not be complete without reference to the excellent process devised by Greenawalt.<sup>10</sup> While this process is very similar in many respects to that used at Ajo, each was developed independently of the other. The Greenawalt process has two outstanding features. These are (1) the continuous reduction of the ferric sulphate with sulphur dioxide by circulating the cell solution in closed circuit with the reducing apparatus, (2) the precipitation of the copper in the discard solution by means of hydrogen sulphide instead of with scrap iron as at Ajo.

This process is applicable to oxidized as well as to roasted sulphide ores. By this continuous reduction feature Greenawalt states that he is able to reduce the copper content of the solution going through the electrolytic cell to a greater degree than with simple reduction as carried on at Ajo.

For the removal of the copper from the solution which must be discarded, Greenawalt uses hydrogen sulphide. This is effective in various acid concentrations and has the advantage of leaving the solution in condition for further use as a lixiviant should this be desired. It is very doubtful, however, if the cost of the precipitation of the copper from waste solutions by hydrogen sulphide is less expensive than precipitation by scrap iron. From tests conducted at Ajo the costs are about the same, while the solubility of the copper sulphide precipitate in dilute ferric sulphate is not appreciably different from that of cement copper.

The main feature of the Greenawalt process is the continual generation of sulphuric acid. The process when operated under proper conditions, may be made self-sustaining. As the cost of sulphuric acid is one of the largest items of expense in leaching, the advantages of this process may readily be seen.

At Ajo, where the ferric sulphate in the solution going to the electrolytic cells is reduced with sulphur dioxide there have been periods when the sulphuric acid produced in the towers alone has been sufficient to carry on the leaching process without the introduction of outside acid.

**Ammonia and Ammonium Carbonate.**—Next to sulphuric acid in importance and efficiency as a leaching agent may be mentioned ammonia and ammonia compounds. In the presence of air, ammonia and ammonia salts react quite energetically with metallic copper and oxidized copper compounds. The active constituent is the cupric ammonium carbonate which is formed and which reacts with the copper minerals, forming cuprous-ammonium carbonate. In the presence of air, the cuprous compound is rapidly oxidized to cupric, and again becomes an active leaching agent. When a solution containing cuprous or cupric ammonium carbonate is heated, both the ammonia and the carbonic acid are distilled off and condensed while the copper is precipitated as a cuprous or cupric oxide. There is no fouling of solution.

This process is said to have been originally developed in Germany.<sup>14 15</sup> In 1871, in a paper read before the A. I. M. E., the matter of native-copper losses in the Calumet & Hecla tailings was discussed and the fact brought out that this copper could be dissolved in solutions of ammonia salts. Some years later when the treatment of these tailings was again considered, ammonia-leaching tests were conducted which resulted in the erection and operation of the present plant, in which some 8,000 tons per day are treated.

The material treated at the Calumet plant is finely divided metallic copper in sands. This metallic copper is at all times covered with a thin film of oxide which is

rapidly dissolved in ammonia in the presence of an ammonia salt. If the metallic copper is again subjected to the air, it will again be covered with a thin film of oxide which will dissolve. These reactions are the basis of the ammonia-leaching process.

The early difficulties of the process are said to have been the loss of the highly volatile ammonia which occurred both during the leaching and during the boiling of the solution. Benedict<sup>14</sup> found that this loss was not solely due to volatilization but to a larger extent to adsorption of ammonia by the ore particles. This loss increased with the strength of solution. By using only a weak solution treating low-grade material and driving off the adsorbed ammonia from the tailings by steam before discharging, Benedict found that these losses could be reduced to a minimum. This process when applied to the Calumet tailings gives an average extraction of about 80 per cent.

At the Kennecott Copper Corporation at Kennecott, Alaska,<sup>16,17</sup> copper carbonate, both azurite and malachite, is found with chalcocite in dolomite and limestone. The ore is treated by milling, whereby most of the sulphide copper and about 60 per cent of the oxidized copper minerals are recovered. The tailings from this milling process, averaging about 1 per cent copper, are treated by ammonia leaching. About 75 per cent of the soluble copper is dissolved.

The original lixiviant consists only of a 5 to 6 per cent solution of ammonia. This soon becomes quite saturated with  $\text{CO}_2$  which increases the time necessary to get a satisfactory extraction. As in the case of the Calumet & Hecla, the principal problems to work out were the recovery of the ammonia and the distillation of the rich copper-ammonia liquors. Other troubles, mostly of a mechanical nature, have been overcome, so that this method of recovering copper is receiving more and more attention, as it is particularly adapted to the many low-grade carbonate ores in which the acid-soluble constituents are so great as to make an acid leach unprofitable.

An ammonia process known as the Perkins process<sup>18</sup> is said to have given excellent results on some of the low-grade ores of the Southwest. This process consists of heating the ore to be leached in a reducing atmosphere, during which all or a large part of the copper mineral is converted into metallic copper. It is then leached with ammonia.

**Ferric Sulphate.**—Ferric sulphate is not only an active solvent of most oxidized copper minerals, but also quite an active solvent of free copper sulphides. Complete extraction is possible on oxides and on carbonates in comparatively short periods, while sulphides are more slowly acted upon. To overcome the resistance of double sulphides, such as chalcopyrite and bornite, to this reagent, a partial roasting was suggested by Thomas. This was found very helpful, and under proper roasting conditions commercial extraction may be obtained from sulphide ores with ferric sulphate as the lixiviant. Heat was found to promote the leaching reaction.

Much careful work has been done with this reagent. Probably the earliest is that of Siemens & Halske, who, in 1890, introduced a process which consisted of leaching an ore ground to 90 mesh with hot dilute ferric sulphate. The copper was precipitated electrolytically, using insoluble anodes and the lixiviant regenerated. The results obtained by Siemens & Halske were disappointing and did not warrant its further introduction. This work, however, is the basis of most ferric sulphate processes. There is no doubt that, had there been available to these investigators the present knowledge of the use of insoluble anodes, diaphragms, tank linings, etc., the results would have been very different.

Among the large-scale tests made with this reagent, probably the more important are those made at Cananea, Sonora, by the Cananea Consolidated Copper Co.<sup>20,21</sup>

and at Ray, Ariz., by Westervelt.<sup>24</sup> At Cananea the principal difficulty encountered appeared to be the regeneration of the lixiviant. At Ray, the raw ore was leached with hot dilute ferric sulphate and the copper was precipitated electrolytically. This later work was practically a modification of the Siemens & Halske process, and, as at Cananea, the regeneration of the solvent appeared to be the principal difficulty.

In heap leaching, as practiced at Rio Tinto, where copper is extracted from massive iron pyrite, the extraction depends upon the action of ferric sulphate. By proper control of the ventilation and the wetting of this ore, ferrous sulphate is formed, which, on further action, changes to ferric sulphate and, as such, dissolves the copper.

The ores treated by leaching by the New Cornelia Copper Co. contained at all times a small quantity of copper as sulphide. The per cent of total oxide and sulphide in both the head and the tailings of each charge treated was carefully determined. During the treatment of some 10,000,000 tons of ore the extraction on the sulphide portion of the ore has been very consistent, varying from 25 to 30 per cent of the copper contents. As it was definitely proved that a pure dilute solution of sulphuric acid has no action on these sulphide minerals, it can be assumed that this leaching action on the sulphide portion of the ore is due to the presence of the small quantity of ferric sulphate contained in the leach solution.

**Sulphur Dioxide.**—Sulphur dioxide is readily absorbed by water, forming sulphurous acid. As such, it is an active solvent of many oxidized copper compounds. It can generally be cheaply and easily secured, as nearly all localities containing copper also contain some sulphur.

Ore containing high acid-soluble constituents are especially adaptable to sulphur dioxide leaching. Copper sulphite is formed. This is unstable and is readily converted into cupro-cupric sulphite and copper sulphate. Cupro-cupric sulphite is slightly soluble in water, but is easily soluble in sulphur dioxide and in cupric sulphate.

The use of sulphur dioxide as a leaching reagent has been very attractive, with the result that much experimenting has been done and many processes have been devised. Of these processes the earliest one is probably that of Neill and Burfield, a patent for which was issued about June, 1902. This process consisted of subjecting the ore to the action of sulphur dioxide to dissolve the copper, removing the solution from the ore and then heating it to drive off the excess of sulphurous acid and precipitate the copper as sulphite.

The process was given a rather extensive trial on the sandstone copper ores of northwestern Arizona,<sup>19</sup> but the work was discontinued before the value of the process was definitely established. The instability of the copper compounds appeared to be the principal difficulty. Joseph Irving, Jr.<sup>25</sup> describes some leaching tests made at the Nevada-Douglas Consolidated Copper Co., where wetted fine ore was brought in contact with hot sulphur dioxide gas. The copper was precipitated upon scrap iron.

Many other commercial or near commercial tests were made along similar lines, but up to this time (1924) there are no large installations of this kind either in process of construction or in operation. That this reagent has many attractive possibilities is, however, generally conceded and the troubles developed will probably be overcome.

This problem was taken up and seriously studied during 1917 and 1918 by the U. S. Bureau of Mines.<sup>20</sup> It is thought that a successful process, compact and apparently inexpensive, has been developed. The operations are simple and readily controlled. They consist of passing a mixed ore pulp through a revolving drum containing baffles to impede the progress of the ore, countercurrent to hot sulphur dioxide gas. The copper is brought into solution during the passage of the pulp through the drum, and is later recovered by either precipitation on iron direct, or by

precipitation on iron and then floating the metallic copper precipitate. The results were most encouraging.

During the development of this process,<sup>21</sup> it was found that the pulp from the treatment of a roasted cupriferous pyrite by this process contained an unexpected quantity of free sulphuric acid. Careful investigation brought out the fact that dilute sulphur dioxide gas had a tendency to oxidize the ferrous sulphate to the ferric state and produce free sulphuric acid. In other words, when ferrous sulphate is agitated under certain conditions with air and sulphur dioxide the ferrous sulphate is oxidized to ferric and free acid is produced. It was found that the free acid concentration so produced could be carried to as high as 5 per cent. This discovery is probably one of the most important contributions to the field of hydrometallurgy in recent years.

**Chlorides.**—Of the various chlorides that have been suggested, ferric chloride is probably the most important, on account of both its cheapness and the ease with which it may be regenerated. It not only has the property of readily dissolving the oxides of copper, but it quite actively decomposes many of the sulphides of copper. Its application as a leaching reagent for copper ores was mentioned as early as 1859.

Ferric chloride, while similar to ferric sulphate in its effect on copper ores, is less apt to form basic salts, and attacks other elements more readily.

Cupric or cuprous chlorides are formed by the action of ferric chloride on copper sulphides, the ferric chloride being reduced to ferrous, and, as such, may be regenerated by oxidation with chlorine.

The Doetsch process, based upon the reaction between ferric chloride and copper sulphides, was once extensively used at Rio Tinto. This process consisted of leaching large heaps of half-inch ore, previously mixed with salt and ferrous sulphate, with a dilute solution of ferric chloride. The ferrous chloride produced during the leaching was converted to ferric by bringing the solution in contact with chlorine gas, in scrubbing towers.

The Froelich process consists of agitating finely ground ore with a warm ferric chloride solution and precipitating the copper with metallic iron.

Both processes have much merit and warrant further investigation.

Ferrous chloride has also been used to some extent as a leaching agent. The most notable application of this lixiviant is in the Hunt & Douglas process.<sup>22</sup> Roasted or oxidized ores were treated with a neutral solution of ferrous chloride and sodium sulphate. As this reagent does not dissolve arsenic, antimony, and various other elements highly objectionable to copper, the precipitate was very pure. This method was later somewhat modified and a comparatively large tonnage of material for that time was treated by this process.

The Hoepfner process, in which cupric chloride was used as a lixiviant, at one time received much attention. The copper is precipitated electrolytically from a cuprous chloride solution, the cupric chloride, which is formed during deposition, is used as the solvent for further copper. The principal obstacle to the success of this process was the tendency of the cupric chloride to dissolve the deposited copper, and the necessity of continual solution purification.

Chloridizing, roasting, and leaching have found quite wide application as the Longmaid-Henderson<sup>23</sup> process and is at the present time the principal process employed in recovering copper from pyrites cinders. The crushed cinders mixed with salt and sometimes with pyrite are treated in special muffle furnaces. The material so treated is then discharged into tanks and leached with water, precipitating the copper with iron.

The advantage of chlorine as a reagent has long been recognized and its intensive action on the ores of the various metals has been also investigated. The principal obstacles in the use of this reagent are mostly mechanical and not chemical. The application of chlorine will find its greatest field in ores carrying, besides copper, precious metal values.

**Nitric Acid.**—The proposal to use nitric acid as a leaching agent is quite old, dating back at least to 1874. The fundamental idea is to employ the nitric acid as a catalyzer to obtain a complete oxidation of the sulphides to sulphates by means of atmospheric oxygen at a comparatively low temperature. The use of nitric acid for decomposing sulphide ores in analytical work is old. It has been proposed to feed finely crushed ore, with the proper proportion of nitric acid, into a rotating furnace, similar to a cement kiln, which is heated near the lower end to a temperature sufficient to expel completely the nitric acid and the oxides of nitrogen after the sulphating reaction is completed. The presence of sulphuric acid derived from the pyritic sulphur will assist the decomposition of any nitrates that may be formed. The sulphated ore was to be leached in the usual way. The nitric acid vapor and lower oxides of nitrogen were to be recovered by a suitable tower and scrubbing system, and converted through the agency of atmospheric oxygen and water into nitric acid. The nitric acid required is directly proportional to the quantity of sulphides in the ore.

The success of this process depends upon minimizing the loss of the nitric acid which may occur in three ways, namely, through the formation of nitrous oxide and free nitrogen, which cannot readily be converted into nitric acid; through the incomplete expulsion of nitrogen compounds from the sulphated ore; and through leakage and inefficiency of the recovery system.

The use of nitric acid as a leaching agent under certain conditions has been patented at various times. Of these, the Rankin process,<sup>22</sup> in which ore is treated with nitric acid in a closed vessel with temperature not over 125°C., is probably the best known. This process was tried out at the Nevada Douglas Copper Co., Ludwig, Nev.<sup>23</sup> The results of these tests were described in detail about a year later.

From all accounts, the nitric acid process is worthy of much consideration, particularly for the treatment of low-grade sulphides as well as low-grade ore containing both oxides and sulphides.

Nitric acid is probably the most active of all solvents for copper ore and will energetically attack both the oxides and the sulphides, but the successful operation of this process will depend upon being able to obtain a high per cent recovery of this rather expensive reagent so as to distribute the cost over sufficient copper to make the process commercial.

**Washing.**—After the copper values have been dissolved from the ore and the solution drained off, there is still present a large quantity of dissolved copper as entrained solution. In some cases this entrained solution may amount to between one-half to one-third of the total copper dissolved from the ore. When an ore has been leached by percolation, this dissolved copper may be recovered in either of two ways (1) by filling the interstices with water and circulating this water, draining and repeating this operation until the entrained copper is negligible; (2) by filling the interstices of the ore with water and then drawing it off at the bottom, keeping the material covered and the interstices filled until the draining shows a negligible quantity of copper. This latter method is called the



"piston method." It is claimed to use less water, require less time and cause less trouble than the first method. The former is the method used at Ajo, the latter is the method used at Chuquicamata.

**Precipitation.**—The methods of precipitating copper from the pregnant acid or neutral solutions are, in the order of their importance: (1) precipitation as the purest form of copper by electrolysis, usually from copper sulphate electrolyte; (2) precipitation as impure metallic copper by some form of metallic iron from sulphate or chloride solutions; (3) precipitation as metallic copper with sulphur dioxide under heat and pressure when applied to sulphate solutions; (4) precipitation with hydrogen sulphide as copper sulphide.

In the processes in which ammonia and ammonium carbonate are used as a lixiviant, the copper is precipitated out of solution by simply boiling off the ammonia. At the present time, the first two, only, are of commercial importance in the treatment of pregnant solutions obtained from acid lixiviants.

**Precipitation by electrolysis** is very similar to electrolytic copper refining. The principal difference is that in the former case insoluble anodes are used and the copper is taken out of the solution, while in the latter case the anodes are soluble and replenish the copper contents of the electrolyte as it is withdrawn.

The resulting product, electrolytic cathodes, is the purest obtainable commercial copper, easily handled, and has only to be melted into shapes to meet commercial requirements. The impurities occurring in refinery solutions are generally more serious than those existing in leaching solutions. Refinery electrolytes are frequently apt to contain arsenic and antimony in quantities sufficient to contaminate the copper. None of the leaching solutions treated at the present time by electrolysis contain appreciable quantities of arsenic or antimony. The impurities which do occur in leaching solutions are readily eliminated by simple fusion.

Copper has been precipitated from chloride and other electrolytes, but not on a large enough scale to warrant discussion. Probably all the copper sulphate leaching solutions containing over a certain per cent copper can be prepared for electrolysis. Its application will depend almost entirely upon the cost of power.

Alumina, iron, magnesia, and sodium are the principal elements besides copper that occur in leaching-solution electrolytes. Of these impurities, the iron, on account of its alternate oxidation and reduction and thereby uselessly consuming current, is the most important one.

When electrolysis is used to precipitate copper from solution, the acid that was combined with the copper is regenerated. The impurities, however, accumulate and must be removed.

This ferric sulphate problem may be remedied in three ways: (1) by the use of a diaphragm or porous partition, so that the ferrous iron that is oxidized at the anode cannot come in contact with the deposited copper at the cathode; (2) by purification of the solution previous to electrolysis; (3) by keeping the ferric sulphate contents of the electrolyte at as low a point as is possible by continual reduction with sulphur dioxide.

*The use of a diaphragm anode as a method of solving the ferric sulphate problem has not been applied on a large scale, principally because no satisfactory commercial diaphragm has yet been developed. While the advantages of a properly constructed diaphragm would be very important, its use would probably be limited to cases in which ferric sulphate is to play the more important part as a leaching agent, as with the simple sulphides of copper.*

*Purification of solution is commercially practical.* Such a method, based on the Ottokar Hoffman<sup>33</sup> process of purifying copper sulphate solutions and applied to the treatment of leach solutions, was tried at Ajo. This process, invented by Pope & Hahn,<sup>34</sup> consisted of treating the ore with two lixiviants, a low and a high acid. The former dissolved much copper and few impurities, the later dissolved the balance of the copper and a greater quantity of impurities. The later solution was purified by heating, and then agitating with air after the addition of sufficient roasted copper concentrates, to precipitate the iron. The solution is filtered, the filtrate added to the first leach liquor, and both electrolyzed. Between 75 and 85 per cent of the total impurities in the electrolyte were removed. These tests were discontinued before the value of this process was definitely proved.

At the present time, the details are being drawn of a leaching and electrolytic plant capable of producing 200,000 lb. of cathode copper per day. This plant will leach an oxidized copper ore with sulphuric acid, purifying the solution before electrolysis by agitating the neutral solution with finely ground ore until the iron and alumina have been precipitated. This method is similar to that proposed in 1914 by Pope and Hahn and tried at New Cornelia.

This method of solution purification was also suggested by E. A. C. Smith in 1897.<sup>35</sup>

The reduction of the ferric sulphate by sulphur dioxide is very simple and is no doubt the cheapest and most efficient way to meet this problem. Its use for such a purpose is not new, having been suggested as far back as 1908.

The application of sulphur dioxide for this purpose on a large scale was quite openly ridiculed. As late as 1914, the engineers on the New Cornelia Copper Co. test plant were advised that reduction with sulphur dioxide on a commercial scale was impossible and were urged to give up this matter. No trouble was experienced except that it was found that, as may be expected, the more nearly neutral a solution is the more easily it may be reduced.

Sulphur dioxide is cheap, the application for reduction is simple, and for each pound of sulphur used in reducing ferric sulphate 3.5 lb. of free sulphuric acid are produced. About 30 to 35 tons per day of ferric sulphate are reduced to ferrous sulphate with sulphur dioxide in the reduction towers of the New Cornelia Copper Co. To obtain this result, some 35 to 40 tons of sulphide ore containing 40 per cent sulphur are roasted to a calcine containing about 6 per cent sulphur. During this operation about a hundred tons of free sulphuric acid are regenerated, or about 75 per cent of the total required by the leaching plant. Under proper conditions the acid produced by the ferric sulphate reduction will be sufficient to carry on the process without the addition of acid from other sources.

The sulphur contents of the gas employed in reduction is not of vital importance, although, naturally the higher the  $SO_2$  the more efficient will be the absorption. The gas used at Ajo has been as low as 3 per cent and as high as 8 per cent with an average of about 5½ per cent for six years of operation. The use of towers for reduction has proved satisfactory. For the entire period of operation, nearly six years, the ferric-sulphate contents of the solution entering the electrolytic tank house will probably average 0.10 per cent or less, while for the past four years the average would be less than 0.05 per cent.

Greenawalt appears to have somewhat improved the process of intermittent reduction as used at Ajo by connecting each set of depositing cells with a sulphur-dioxide reducing apparatus. In this manner, the ferric sulphate is reduced nearly as fast as it forms and the continually increasing acid contents to some extent compensates for the decreased copper contents in the resistance of the cell, and more copper can be deposited per cycle than at Ajo.

In the Greenawalt process rapidly revolving discs, the peripheries of which just touch the surface of the solution and thereby produce a continuous quantity of exceedingly fine spray, are used in place of towers for reducing purposes.

The electrolysis may be carried on in either lead-lined or asphalt tanks. The former are used at Ajo, the latter at Chuquicamata.

Lead anodes are used where the solutions contain neither chlorides nor nitrates. After nearly six years of continuous operation the antimonial-lead anodes in use at Ajo have shown but little loss in weight. At Chuquicamata, where the solution contains both nitrates and chlorides, a fused magnetite anode was first used. When the World War made these unobtainable, ferrosilicon was successfully used. Later a copper-silicon-lead anode<sup>36</sup> was developed, which has proved still more efficient.

Carbon or graphite anodes have not been used on a commercial scale for this purpose. One pound of copper per kilowatt-hour has been the average efficiency obtained when using lead or antimonial lead anodes.

**Iron Precipitation.**—In solutions of low copper concentration, too high in impurities for electrodeposition, some form of iron is generally used for precipitation purposes. When metallic iron is immersed in a solution containing copper, the iron is dissolved and metallic copper is precipitated. The product of this reaction is known as cement copper.

Metallic iron has many advantages as a precipitant; it is generally quite cheap, readily obtainable, and simple to use. Clean iron as a precipitant will, with proper operating care and conditions, produce a high-grade precipitate. The usual 30 to 60 per cent copper contents of cement copper is neither necessary nor is it good practice.

There is theoretically required 0.878 lb. of iron per pound of copper to be precipitated, provided no other iron-consuming constituent is present in the solution. Both ferric sulphate, by its reduction to ferrous sulphate, and sulphuric acid, by its action to form ferrous sulphate, consume iron when present in the solution.

Due to the impurity of the iron, consisting of the constituents of the metal other than iron and the adhering iron oxide scale which is nearly always present, as well as the iron-consuming constituents of the solution from which the copper is precipitated, the consumption of iron per pound of copper is generally about 1.5 to 2.0 lb. instead of the theoretical 0.88 lb.

For good precipitation purposes, the solutions should be of as low density as possible; they should be clear, that is, all sand and slimes should have been settled out; the iron should be of as good grade as possible, and clean. The speed with which the reaction takes place depends, of course, upon the surface of iron exposed to solution. Pig iron acts the slowest and sponge or powdered iron the quickest. Therefore much work has been done on the development of a sponge-iron process. This process would consist of reducing the iron in iron ore to metal in a finely divided state and without fusion.

The most important results were obtained at the Chino Copper Co., where a special furnace was developed for continuously producing sponge iron.<sup>49</sup> Here a magnetite concentrate is heated with a partly coked coal in a gas-tight furnace in which the charge is heated by radiation.

Since the development of this furnace, the U. S. Bureau of Mines has announced the development of a similar process, the reduction, however, taking place in a revolving Bruckner-type furnace, very similar to that used at Anaconda also for sponge-iron tests.

Notwithstanding the fact that much work has been done on sponge iron, there are, with the possible exception of the sponge-iron furnace at the Chino Copper Co. plant, no plants in successful and continuous commercial operation at this time.

Both heat and agitation are aids to precipitation. Fine material, such as sponge or shot iron, will permit of agitation, while precipitation with loose or baled scrap, or with pig iron, must be carried on in launders.

With a clean detinned scrap iron, the Ohio Copper Co. has produced some 8,000,000 lb. of cement copper, which has averaged over 90 per cent of copper. Several lots, consisting of 50 or more tons each, have averaged over 95 per cent copper. These are the results obtained when using clean solution of low density and with proper supervision. The average copper contents of all the cement copper produced at Rio Tinto, where pig iron is used, is 75 per cent. At New Cornelia, where baled scrap is used, it is 60 to 65 per cent.

The chemical precipitation of copper by iron is nearly always carried on in either a sulphate or a chloride solution. In either case, it is quite necessary to reduce the ferric salts before precipitation. This may be done by passing the solution over copper or iron sulphides.

The statement frequently made that the acid must be neutralized before the copper will precipitate is not entirely correct. Precipitating copper from waste solutions on scrap iron is frequently done at copper refineries. These solutions sometimes contain as much as 15 per cent acid and the copper may be entirely precipitated without complete or nearly complete neutralization of the acid.

The cement copper commercially produced contains 20 to 30 per cent water or solution. Where this material has to be transported a long distance, drying might prove economical. When drying the material, however, it oxidizes. When it is very dry, it causes trouble by dusting. Tests on drying cement copper showed, when slowly dried to 15 per cent moisture, that 60 to 70 per cent of the copper contents had been oxidized. Whether dried in air or by heat, the quantity of copper oxidized appeared about the same. Air drying is too slow to be commercial. Drying with moderate heat is probably best. The statement that cement copper in drying oxidizes so quickly as to cause spontaneous combustion could not be proved.

The disposal of this cement copper has been the cause of much discussion. Producers of this material frequently have visions of greater profits by converting this cement copper into electrolytic cathodes, casting copper, blue vitriol, or some other more profitable forms. The eventual treatment of this class of material, when in sufficient quantity, will be simple melting or fusion in a coal or oil-fired reverberatory and, perhaps, then tapping molten copper into a refining furnace and subsequent refining so as to produce a casting copper or anodes for the electrolytic refinery. Such an operation should not cost over \$10 per ton and would not require a large expenditure.

The advantages of electrolytic copper in the making of alloys and bearing metals is more and more appreciated and the market for casting copper is becoming more irregular and fluctuating, with the result that direct uses for secondary coppers are becoming less, thus reducing the field for casting copper. In all probability, the most economical disposal of this material will be smelting and casting into cathodes and shipment to the refinery.

**Hydrogen Sulphide.**—Hydrogen sulphide may be considered the next best precipitant for copper from leaching solutions. If hydrogen sulphide is applied to a copper sulphate or copper chloride solution, copper is precipitated as cupric sulphide and acid is regenerated equal to that combined with the copper. This regenerated acid may be used to dissolve further copper.

Hydrogen sulphide may be generated in various ways, the cheapest probably being by the action of sulphuric acid on a low-grade copper matte. Tests made with hydrogen sulphide generated from sulphuric acid and low-grade matte have given the costs of precipitation to be equivalent to iron at \$20 per ton, or about 1 ct. per pound of copper.

Greenawalt recommends hydrogen sulphide for the precipitation of copper from discard solutions. There are no leaching plants in operation at this time where this gas is used as the precipitant of the copper from solutions.

**Sulphur Dioxide.**—The most interesting process that has been developed for copper precipitation is that of George D. Van Arsedale,<sup>37</sup> who found that, when a solution containing copper and ferrous sulphate is saturated with sulphur dioxide and is then heated under pressure, a reaction occurs resulting in the precipitation of about half of the copper as finely divided metallic copper together with the formation of free sulphuric acid. This process has been tried at several plants and it was found that between 60 and 70 per cent of the copper could be quite economically precipitated. The principal difficulty was how to recover the remainder.

This patent of Van Arsedale was followed by several others, all based on the same reaction, but none of them have so far been introduced into large-scale operation.

**Commercial Leaching Installations.**—The most important copper-leaching plants now in operation are those of the Chile Copper Co. and the New Cornelia Copper Co. on sulphuric acid leaching; the Calumet & Hecla Mining Co. and the Kennecott Copper Co. on ammonia leaching; the Ohio Copper Co. of Utah on leaching in place; and the Rio Tinto Copper Co. on heap leaching.

Details on the operation of the Chile Copper Co. are quite meager. It is important to note that between 10,000 to 15,000 tons per day of low-grade ore are treated by this process.

**The Chile Copper Co.**—The ore treated by the Chile Copper Co. at Chuquicamata, Chile, consists of oxidized minerals in seams and fissures affording simple and rapid extraction. The ore contains among other minerals the unusual basic copper sulphate or brochantite. The mineral is readily soluble in dilute sulphuric acid and introduces copper sulphate into the solution which, on electrolysis, liberates free acid. The mineral is reported frequently to be present in sufficient quantity to make the addition of acid from outside sources unnecessary.

The process as applied at the Chile Copper Co. was developed under the direction of E. A. Cappelen-Smith from the results derived from the operation of a 15-ton leaching plant at Perth Amboy, N. J. The details were so clearly worked out in this small unit that the results that are now obtained on the large plant are substantially duplicates of those obtained in the test plant.

The ore, averaging about 1.7 per cent copper, is mined with steam shovels at the rate of 15,000 to 20,000 tons per day, loaded on cars, and transported by rail to the crushers. Successive crushing operations reduce the steam-shovel size so that 30 to 90 per cent will pass 0.371-in. mesh.

Belt conveyors deliver the crushed ore to a traveling bridge, from which it is discharged into one of six reinforced-concrete tanks lined with asphalt, 150 ft. long by 110 ft. wide by 16 ft. deep, set end to end and holding about 10,000 tons each. The ore is charged into one end of the tank until the top of the tank is reached and the bridge is then advanced at such a rate as to keep the level constant. This method of charging a tank classifies the ore so that the coarsest material will be at the bottom and the finest on top.

When the tank has been filled with ore, the first leaching solution is introduced by upward percolation. The ore remains in contact with the solution for 24 to 36 hr., when it is drawn off and replaced by downward percolation with other solutions.

A certain quantity of each solution coming from the ore is removed for the complete deposition of the copper, in order to take care of the impurities and to compensate for the introduction of wash water to the system. The impurities at Chuquicamata consist principally of the sulphates of magnesium, sodium, and potassium, together

with a small quantity of nitrate and chloride. The former, while not detrimental to the operation, would accumulate to such a point as to render the solution inactive. The chlorides and nitrates go into solution with the copper and must be eliminated as far as possible. The chlorides are removed by agitating the pregnant solution in the presence of metallic copper, whereby the chlorine will be precipitated as a more or less insoluble cuprous chloride. About 85 per cent of the chlorine is removed in this manner and about 1 ton of solution is dechlorinated per ton of ore treated. Both chlorides and nitrates when present in appreciable quantities prevent the use of lead anodes.

The ore is ideal for leaching, the extraction obtained averaging consistently over 90 per cent. It has been said that each ton of ore contains between 20 and 30 lb. of what might be called latent acid.

The pregnant solution after dechloridizing is sent to the electrolytic tank house for precipitation. These tanks are of reinforced concrete. There are 894 cells in operation. Lead anodes were at first tried in the experimental plant but were not found satisfactory. A German anode made of fused magnetite was then used. The war with Germany made these difficult to obtain and a ferrosilicon alloy was substituted. Later these were replaced by a special copper-silicon-lead<sup>76</sup> anode developed by the research department of this company. This has proved to have a low counter e.m.f. and is better than any of the previous forms.

Power for all operations is generated at a plant built on the coast, some 150 miles from the mines. Of the total power generated, a little over 80 per cent is used for copper deposition. About 0.85 lb. of copper are deposited per kilowatt-hour to the tank house. Refining furnaces have been provided and the cathodes are melted and cast into commercial shapes at the plant, the product leaving Chuquicamata as the highest grade of electrolytic copper.

This process is being successfully applied to some four or five million tons per year, turning out at practically one continuous operation some 180,000,000 lb. of refined copper from an ore that could not be treated by any other known method.

**New Cornelia Copper Co.**—About the time that the Chuquicamata plant of the Chile Copper Co. was ready to begin operations, the details of the process to be used in treating the ores of the New Cornelia Copper Co. at Ajo, Ariz., had been practically decided upon.

The problem in Ajo differed from that in Chile in that the ore to be treated (1) was of a lower grade; (2) did not carry any latent acid compounds, such as basic copper sulphate; (3) was less readily soluble. On the other hand, the problem at Ajo was simpler. There were neither chlorides nor nitrates to contend with in the ore. Tests could be carried out on a larger scale and closer to the scene of actual operations, supplies were less expensive, and more easily attained.

The location of the deposit, mode of occurrence, and the preliminary tests leading to the development of the process that has successfully treated some ten million tons of ore have all been so often described that only a general discussion will be given here.

After a period covering nearly three and a half years and during which some 15,000 tons of ore were treated, a process was developed, the results of which would be positively foretold.

The process adopted was as follows: (1) mining by steam shovels, the maximum size to be controlled by the size of a fragment that will pass the shovel dipper; (2) transportation of the ores in cars that will stand up to the rough service and discharge freely any fragments that passed through the dipper of the steam shovel; (3) the delivery of the ore, without any storage other than cars, directly into a crusher that

will receive any fragment discharged by the car; (4) crushing of steam-shovel size to as near  $\frac{1}{4}$  in. as practicable; (5) leaching the crushed ore 8 days by a counter-current system and upward circulation, using sulphuric acid and such ferric sulphate as is inherent in the process; (6) reduction by sulphur dioxide gas of the ferric iron remaining in the neutral solutions from the leaching tanks; (7) the electrolytic deposition of part of the copper from this reduced solution, which is then returned to the leaching solution; (8) the continuous discharge of such portion of the neutral solution as is necessary to prevent accumulation of sulphates other than copper to the saturation point; (9) the recovery of the copper content of such discarded solution as cement copper precipitated on iron; (10) the treatment of a part of this cement copper with solution from the electrolytic tank house to the end that the copper be returned to the circulation and a part of ferric sulphate reduced.

**Crushing.**—The ore is mined by steam shovels and is loaded and delivered to the crushing plant in side-dump cars. The crushing plant is divided into two departments, coarse and fine, which are separated by a 10,000-ton storage bin.

The 10,000-ton storage bin between the coarse and fine crushers is of steel, built on an elevated reinforced-concrete platform. The ore is drawn from it automatically onto a set of five belt conveyors, equipped with magnetic head pulleys, which deliver the ore to five units of Symons vertical-shaft disc crushers. Each unit consists of three interchangeable crushers. The first is set to crush to inch cubes. The crushed material is elevated and screened; the undersize by-passes the remaining two crushers, which are set in parallel. The oversize passes to these two crushers, which are set to crush to the desired size. The entire product is fed to a system of belt conveyors, which lead through a sampling plant to the leaching vats, which furnish the only storage for the crushed ore.

**Leaching.**—The leaching tanks, 88 ft. square and 17 ft. 4 in. deep inside, are built of reinforced concrete with wooden bottoms. Each has a capacity of 5,000 tons of crushed ore. The sides and the launders of the tanks are lined with 8-lb. lead and the bottom with 6-lb. 4 per cent antimonial lead. The filter bottom is laid over the lead bottom and consists of 5- by 12-in. joists on edge laid on 16-in. centers, covered with 2-in. ship-lap planks that are bored with  $\frac{3}{8}$ -in. holes on 2-in. centers countersunk from below. Under the center of the filter bottom, and at right angles to the wooden floor joists, a distributing launder is set in the floor, through which the solution enters and from which it is distributed under the filter bottom. The lead lining on the sides of the tanks is protected from abrasion by a covering of 2-in. planks. At the top and sides of each leaching tank are two overflow launders extending the length of the tank, one end being connected with the suction of a circulating pump. The charging is done by a machine especially designed for this plant and known as the spreader bridge. It consists of a traveling bridge of structural steel which spans the tanks and travels, as desired, lengthwise with the row. The bridge supports a belt conveyor, which receives the crushed ore from the belt on a central structure. A tripper on this belt spreads the ore in the leaching tanks.

The tanks are charged by filling to the top of the tank at one side, allowing the ore to assume its natural slope, or about 45 deg., and then continuing at one side and discharging the ore at the top of the slope, allowing the coarser material to run to the bottom and the finer to remain somewhat higher up, thus giving a rough classification. The bridge is moved slowly forward as the filling of the tank progresses. This plan

was suggested by the engineers of the Chile Copper Co., who have obtained the best results through this method of filling.

The crushed ore is leached from 6 to 8 days by a countercurrent system and upward percolation, using dilute sulphuric acid as the principal solvent.

The solution in each tank is circulated by two 15-in. vertical centrifugal pumps having a capacity of 3,500 gal. per minute each. These are driven by direct-connected 40-hp. vertical motors. The head against which the pumps work is equivalent to the friction head of the solution passing through the ore. The discharge from one of these pumps is provided with a by-pass which permits a portion of the solution to be advanced to the next tank. Both pumps are throttled to give a circulation of about 4,000 to 5,000 gal. per minute through the ore. Of this amount about 1,000 gal., called the solution advance, is continuously passing through from tank to tank. The high-acid solution, which has averaged about 2.5 per cent free acid for an 8-day leach, coming from either or both the tank house and the solution storage, and going on the oldest ore, is called the 'acid advance.' The nearly neutral solution coming off the newest charge and going to the reduction towers is known as the "neutral advance."

Upon the entrance of a new charge into the circuit the solution remaining in the oldest tank is drained to the solution storage, where it is standardized with acid and is later used as acid advance. After thorough draining the tank is ready for the wash water.

As the copper entrained in a charge after leaching is about one-third of the total copper dissolved, the question of thorough washing is very important. Four successive wash waters with drainings are used.

The fourth wash of any one charge is used as the third wash of the succeeding charge, the third used as the second and the second as the first. In other words, each wash water is used four times, the copper contents increasing each time, when it is incorporated into the system to make up the continuous losses of solution. These losses are due to evaporation, discard, and solution entrained in tailings.

After a charge has been washed and drained, the tailings are removed from the tank by a Hulett unloader, similar to unloaders used on the Great Lakes for unloading iron ore from boats. A heavy steel bridge on trucks spans the leaching tanks and travels their entire length. On this bridge travels a trolley carrying a walking beam, bucket leg, and bucket of 12 ton capacity. The unloader has a rated capacity of 500 tons per hour and will generally excavate a tank of tailings in 10 to 11 hr.

**Reduction of Iron.**—In the electrodeposition of copper from a sulphuric acid solution, iron, if present, will consume electric energy, by its alternate oxidation and reduction, thereby reducing the quantity of copper deposited per unit of current. During the experimental work the control of the ferric iron proved one of the hardest problems to solve. A patent diaphragm anode was tried and gave good results, but was cumbersome and difficult to keep in order. Later, tests made on a process in which iron and alumina were precipitated as hydrated oxides by the addition of roasted copper ores gave good results. This method was considered too complicated for an ore of this character. The idea was then suggested of using the natural oxides and carbonates in the ore itself as the precipitant of the ferric sulphate; in other words, the precipitation of the principal impurities in the solutions upon the charge itself. Early tests made on a small scale were very promising, but tests carried out later on a larger scale failed to give the desired results. For the first 15 or 20 days, the copper in the newest charge of ore was sufficient to precipitate all the ferric iron that was contained in the solution passing through the ore. However, as the acid concentration on each charge increased, the precipitated ferric iron was redissolved and eventually



accumulated to such an extent that the iron in the solution was in excess of the copper available as a precipitant.

It was now decided to resort to  $\text{SO}_2$  reduction. The general opinion was that this was both unsatisfactory and difficult. This proved to be the case in solutions decidedly acid, but where neutral or slightly acid solutions were used, reduction proved quite easy. For these tests elemental sulphur was used, as it was believed that a gas with the maximum percentage of  $\text{SO}_2$  was most essential and that a rich gas could only be produced by burning elemental sulphur.

In the sulphite-pulp industry large quantities of sulphur gas are produced and absorbed, and, accordingly, the method of producing and absorbing the gas used in that industry was investigated. It was found that at some plants pyrites were used and that under proper conditions a gas of 12 per cent  $\text{SO}_2$  could be produced. The only objection in the sulphite-pulp industry to the use of pyrites was the tendency of small calcined particles to be carried into the solution and thence into the pulp. Upon investigation it was decided to make use of the cheap and abundant supply of the high-sulphur low-copper ores of the Bisbee district.

A bucket elevator and a conveyor equipped with automatic tripper delivers the crushed ore to hoppers situated above four Wedge roasters. These roasters are 22 ft. 6 in. in diameter, have seven hearths, and are belt driven by  $7\frac{1}{2}$ -hp. motors.

The gas leaving the roasters enters the spray or cooling chamber. This chamber is 14 ft. square, 94 ft. long, and is built of 8-lb. lead supported on a wooden framework. Nozzles are distributed over the top and sides through which "neutral advance" is sprayed to cool the gas before it enters the towers. Between 90 and 100 gal. of solution per minute are required to supply these sprays. The ferric iron in the solution used in cooling the gas is practically all reduced and the solution joins that coming from the towers. The temperature of the gas in its passage through the spray chamber is reduced from 600 to 150°F. A flue connects the spray chamber with the bottom of the first pair of towers, dividing the gas equally between them.

There are six towers arranged in pairs. Two pairs of the towers are part of the original equipment and are 40 ft. high and 20 ft. in diameter. These are built of sheet lead, supported on a steel framework. The other pair are 28 ft. in diameter, 40 ft. high, and are built of ordinary redwood tank construction, hooped together with iron rods. As an additional precaution against gas leakage, the wooden towers are painted with asphalt and covered with roofing paper under the hoops. The towers rest upon a reinforced-concrete base, provided with a lead pan. All towers are filled with boards placed on edge, the width of a board apart, and in layers. Each layer is laid at right angles to the one immediately below it. The solution is distributed over the top of the towers by a system of launders provided with gas seals. Between the second and third pair of towers is a fan which draws the gas from the roasters through the spray chamber, and a third set of towers, and forces it through the second and first sets to the atmosphere. The temperature of the escaping gas is that of the atmosphere.

The solution (or neutral advance) to be reduced travels countercurrent to the flow of gas, that is, the most reduced solution comes in contact with the strongest gas. The solution coming from the newest tank of ore is pumped to the top of the third pair of towers by a centrifugal pump. The solution distributed by launders and gas seals flows down over the filling, thus coming into intimate contact with the rising gas. At the bottom of each pair of towers there is a concrete lead-lined sump, into which the solution flows and is then pumped through the next pair of towers. From the first pair of towers the solution is pumped to the second pair, then to the third pair, and then to the so-called settling tank, whence it goes to the tank house. The purpose of this settling tank is twofold: one, to settle out the slime; the other, to get the benefit of the additional reduction that was found to take place in a neutral or slightly acid solution on standing.

**Electrolytic Deposition.**—The electrolytic tanks are housed in a structural-steel building, 166 ft. wide and 280 ft. long, having sides only partly enclosed to give good ventilation. The tanks are all on the same level, none in cascade.

The cellar, which is open on all sides, has an asphalt floor draining to gutters that lead to a sump at each end of the building. There is head room throughout the cellar to permit regular inspection of tanks, piping, and feed wires.

The electrolytic tanks are arranged in banks with aisles between. There are twelve banks of ten tanks each and four banks of eight tanks each, making a total of 152 tanks. Each tank is separated from the adjacent tank by a 3-in. air space. All tanks are made of Oregon pine, lined with 7-lb. chemical lead. The inside dimensions of the tanks are 29 ft. 7 in. long, 4 ft. 9 in. wide, and 4 ft. 3 in. deep. These tanks are supported on concrete columns, and are insulated by tile blocks covered with sheet-lead caps. Each tank is provided with a 4-in. clean-out plug. There are also two perforated lead diaphragms, one at each end of the tanks, to assure a uniform circulation. The inlet to each tank is fitted with a 3½-in. diaphragm valve and a 3½-in. glazed stoneware gooseneck for insulating purposes. At the outlet end there is a lead overflow pan fitted with a 4-in. tile pipe suspended in a 10-in. lead boot connected to the discharge pipe.

Each tank has 84 anodes, making a total of 12,768 in the tank house. The anodes are of lead containing 3.5 per cent antimony. The average weight of a lead anode is 215 lb. They are 40 by 51 by ¼ in. thick, and are suspended by two ¼- by 1¼-in. copper bars secured to the tops of the anodes. The submerged surface of all anodes is 41 by 41 in. The spacing of anodes is 4½ in. on centers. The distance from the bottom of an anode to the bottom of the tank is 8 in., while that of the cathode is 7 in. Short circuits are prevented to some extent by providing the anodes with eight chemical glazed-porcelain insulators distributed over the anode faces.

Much doubt was expressed about the life of the lead anode and some very positive statements were made regarding their probable length of life. Continuous service extending for over a year has failed to show appreciable oxidation.

There are 77 cathodes to a tank, or 9,779 cathodes in the tank house, exclusive of starting-sheet blanks. The cathodes, which are 42 in. square, are totally submerged. They are suspended upon copper bars by loops made from starting sheets. The original starting sheets weighed about 15 to 18 lb., while the finished cathodes weigh 130 to 140 lb. At present 127 tanks are used for making cathodes and about 14 to 16 days are required to produce cathodes of the desired weight.

One section of eleven cathodes is removed at a time and carried to the center aisle, where they are washed with hot water to remove the salts and soluble copper. They are then landed on an iron frame to facilitate the hand trucking to the freight cars. Each car is sampled by drilling every twentieth cathode in the center and in diagonally opposite corners. All electrolytic copper, whether cathode or scrap, is shipped to a refinery, where it is melted, brought up to pitch, and cast into commercial shapes.

The cathodes produced have varied from 99.15 to 99.85 per cent in copper content, the impurities being principally slimes, held by mechanical entanglement. The greater the density of the electrolyte the lower is the copper content in the cathodes, and the greater the insoluble matter, iron, and alumina. The cathodes always contain more or less chlorine, varying from 0.05 to 0.35 per cent. There being no arsenic or antimony in the ore, and very little in the acid, the average arsenic content of the anodes is less than 0.0015 and the antimony less than 0.0005 per cent.

Twenty-five tanks operate on starting sheets, each tank containing seventy-seven starting blanks, or a total of 1,925 blanks. The starting blanks are of rolled 3.5 per cent antimonial lead, 53 by 43 by ¼ in., and are large enough to allow a small amount

of trimming, which is done with a squaring shear. The anodes in these tanks are 3.5 per cent antimonial lead, and are 41 by 52 by  $\frac{1}{4}$  in. They do not have porcelain insulators, as these tend to spot the starting sheets. The spacing of anodes in these tanks is the same as in the commercial tanks. The tank construction and other details are likewise similar.

Eleven blanks are handled at one time by the crane, and placed on an iron stripping rack provided with a crawl so that the blanks can be carried, one at a time, to the center of the rack, where the starting sheets are removed by two strippers, one stripping from each side. After stripping, the blanks are oiled and placed on the opposite end of the rack to be returned by the crane to the tanks.

The electrodes hang parallel to the flow of solution (or parallel to the length of the tanks) to give a free circulation of the electrolyte. This method of hanging the electrodes was first brought to our attention by the work done at the Butte & Duluth leaching plant.

Alternate bus bars extending across the tanks connect the electrodes in parallel and the tanks in series. These bus bars, placed across the tank, divide it into seven sections or cells. The intermediate bus bars are  $1\frac{1}{2}$  in. wide and 4 in. deep, while the end bus bars are 1 in. wide and 4 in. deep. Soldered along the top of each bus bar is a triangular piece of copper,  $\frac{1}{2}$  in. high, giving a point contact to the electrode bars. Small maple blocks impregnated with linseed oil insulate cathodes and anodes from opposite bus bars. These bus bars are supported on insulated iron castings, which, in turn, rest on the tank elements. The current for the deposition of the copper is supplied to the tank house by two identical 15,000-amp. circuits, each circuit having seventy-six tanks in series. This arrangement gives the maximum current density of 8 amp. per square foot of cathode surface when operating under normal conditions. With an average current efficiency of 80 per cent this means a daily gain of about 10.25 lb. per cathode, or a total capacity of 120,000 lb. of electrolytic copper per day. The drop of potential between anodes and cathodes has averaged very close to 2.00 volts. There is a tendency for the voltage to drop during the summer due to an increase in the temperature of the electrolyte.

The solution flow in the tank house is part of a closed circuit with the leaching and reduction plant, receiving a continuous flow of solution from them. This flow, coming always off the newest ore, then through the towers and settler, is regulated by means of weirs and has varied from 800 to 1,500 gal. per minute, depending on operating conditions. This volume is divided among the sixteen banks of tanks, those on starting sheets getting generally a little more than those on cathodes. By this arrangement each bank of tanks on cathodes receives between 60 and 70 gal. per minute of reduced solution. Each bank unit consists of either eight or ten tanks, a sump, and a 9-in. vertical-type centrifugal pump having a capacity of 1,600 gal. per minute. Each bank has an individual circulation of 1,600 gal. per minute between it and the sump, while an overflow arrangement provides for the return of such a portion of the electrolyte as is equivalent to reduced solution added.

The current efficiency depends on the quantity of ferric sulphate present, due to the reaction between ferric sulphate and metallic copper. The ferric iron content in the solution is kept as low as possible and the conditions shown are as good as can be expected. No doubt, with a smaller quantity of total iron present in the solution less would be oxidized, and it was recommended that the total iron be kept below 2 per cent. With the total iron not over 2 per cent, the ferric iron in the electrolyte will probably not exceed 0.5 per cent, the current efficiency will be increased, and more acid will be regenerated.

At the beginning of operations in the tank house, a great deal of difficulty was encountered by the dropping of cathodes in the electrolytic tanks, due principally to the corrosive action of the ferric sulphate on the loops at the solution level, and on

that part of the cathode covered by the ends of the loops. Corrosion at the solution line was easily remedied by raising and lowering the solution level in the electrolytic tanks, but the corrosion of the cathode sheet between the loop ends was far more difficult to overcome. Later this condition became worse with the increase in the ferric iron and higher temperature of the electrolyte. The dropping of cathodes not only caused bad short circuits in the tanks, but also made it necessary, when pulling cathodes for shipment, to pull individual sheets with tongs, which made it almost impossible to handle the daily output of cathodes. Considerable damage was also done to the lead lining of the tanks and the danger from accidents was more than usual. Numerous schemes to overcome this difficulty were suggested and tried, until it was found that, by splitting the ends of the loop and attaching them with a Morrow machine in such a manner that the portion of the starting sheet adjacent to the loop was exposed to the deposition of copper, not only the loop, but also the sheet built up, making a good firm joint. Since the adoption of this method no further trouble has been experienced with dropping sheets. Patents have been applied for and allowed covering this improved loop.

As previously mentioned, only about 45 to 50 per cent of the total acid used in an 8-day leach is utilized in dissolving copper. The remainder is used in dissolving impurities. If copper only is removed from the solution, the other substances will gradually accumulate and the solution will reach a condition where it will become sluggish in dissolving the copper from the ore. To keep the solution active, it is evident that a portion must be discarded and replaced with fresh water. The quantity of solution discarded per day must contain impurities equivalent to the amount dissolved per day, if the accumulation is to be avoided. In the experimental work it was found that, under similar conditions, nearly all the substances that went into the solution were present in a fairly constant ratio to one another. Of the various impurities dissolved, iron is the most easily and quickly determined and was used as the indication of the quantity of solution necessary to be discarded. The experimental work clearly demonstrated that the best results are obtained when the total iron in the solution does not exceed 2 per cent.

The original cementing equipment consisted of six sections of reinforced-concrete launders. These are arranged in two parallel rows of three sections each. The bottom of each launder slopes toward three side clean-out gates. The scrap iron rests upon a grated wood floor. The solution flows through each one successively, but may be by-passed to allow the cleansing and refilling of any of the sections. From these launders the waste solution was to go to the desert.

Under good operating conditions practically all the copper is precipitated. When a launder is no longer efficient, the solution to that launder is by-passed and the solution remaining in it is drained. The cement copper is shoveled out onto wooden grates, where the iron is washed off with a hose, and the unconsumed iron is returned to the launders.

Cement copper when clean and finely divided dissolves readily in ferric sulphate, with the formation of copper and ferrous sulphates. By so doing not only is the cement copper dissolved, but the ferric iron is reduced also. The plan was to hose off the loosely adherent copper from the scrap iron to the bottom of the tank and then flush it into one or more circular lead-lined tanks, called agitators. These tanks are 20 ft. in diameter and 6 ft. deep, provided with a stirring device, driven by a small motor; 125 gal. per minute of tank-house return solution can be circulated through each tank.

This plan of redissolving the cement copper is carried out when the operating conditions of the plant require it. The principal objections to the continuous use of such a plant are that, by redissolving the cement copper in tank-house solution the total copper output of the plant is reduced, which at times does not give the greatest profit possible. It is of interest that somewhat over 12,000,000 tons of ore have been

successfully treated by this process by the New Cornelia Copper Co , during which time approximately 200,000,000 lb of electrolytic copper were shipped as cathodes and 25,000,000 lb of copper shipped as cement copper.



## CHAPTER XXXI

# ELECTROLYTIC REFINING OF LEAD

BY WALTER C. SMITH<sup>1</sup>

**Early History.**—One of the earliest attempts to refine lead electrolytically was made in 1878 by Prof. N. S. Keith,<sup>2</sup> who employed an electrolyte containing 180 g of sodium acetate per liter, in which was dissolved 18 to 22 g of lead sulphate. His anodes weighed about 20 lb, were 15 by 24 in and  $\frac{1}{8}$  to  $\frac{3}{16}$  in thick, and were wrapped in muslin cloths to catch the anode slime. The refined lead crystals dropped off the cathodes and fell to the bottom of the tanks.

At Rome, N. Y., a plant having a capacity of 3 tons per day was operated for a time. Thirty circular concrete tanks 6 ft in diameter and 40 in deep were provided. Each tank had a central pillar 2 ft in diameter, and was equipped with cylindrical brass cathodes. The anode plates measured 6 by 24 in and weighed 8 lb each, 270 anode plates were used per tank. They were hung from a rotating frame and carried scrapers which removed the deposited lead from the cathodes. The current density was approximately 3.2 amp per sq ft of cathode surface. An Edison dynamo of 2,000 amp and a capacity of 10 volts supplied the current.

Tommasi<sup>3</sup> proposed to refine lead, using an acetate solution as the electrolyte and a rotating disc of aluminum bronze as the cathode. The cathode rotated once per minute, and the spongy lead deposit was scraped off the cathode as it came above the level of the tank. L. Glaser<sup>4</sup> made a series of experiments with a number of different electrolytes, and claims to have secured a solid lead deposit. A. G. Betts<sup>5</sup> repeated Glaser's work and could not get a solid deposit. Betts then tried to refine lead, using fluosilicate electrolytes of different strengths, but in every case the cathode deposit was incompact. He tried to compress the deposited lead on the cathode by removing the cathodes from the tanks every few hours and passing them through a set of rolls.

Betts later found that the addition of small amounts of certain materials to a fluosilicate electrolyte caused the production of a solid lead deposit, gelatin, glue, pyrogallol, saligenin, and resorcin gave good results with the fluosilicate electrolyte, but did not improve the deposit from acetate electrolytes. Gelatin and glue were found to be the cheapest and gave the best results, as little as 1 part of gelatin to 5,000 parts of solution gave a solid cathode deposit having the same specific gravity as cast lead. Betts also found that certain acids, such as fluosilicic, fluoboric, dithionic, fatty sulphuric acids, as ethyl-sulphuric acid, phenol-sulphonic, and benzene-sulphonic acids, gave soluble lead compounds and made electrolytes of high electrical conductivity. Mather<sup>6</sup> proposed to use perchloric acid with organic addition agents.

**Electrochemical Data.**—The amount of lead deposited per ampere-hour at 100 per cent current efficiency is 3.8590 g, which is equivalent to 0.20418 lb.

<sup>1</sup> Chemical and metallurgical engineer, Baltimore, Md.

<sup>2</sup> WATT and PHILIP, "Electroplating and Electrorefining."

<sup>3</sup> *Compt. rend.*, **122**, (1896), 1476; *Z. Electrochem.*, **2**, 92, 310, 341.

<sup>4</sup> *Z. Electrochem.*, **7**, (1900), 365-369, 381-386.

<sup>5</sup> BETTS, A. G., "Lead Refining by Electrolysis," 1908.

<sup>6</sup> *Proc. Am. Electrochem. Soc.*, **17**, 261.

per ampere-day, and 204.18 lb. per kiloampere-day. The approximate e.m.f. of solution of the different metals usually associated with lead for fluosilicate solutions is given in the following table <sup>1</sup>

	VOLTS		VOLTS
Zinc	+0 52	Antimony	-0 44
Cadmium	+0 16	Bismuth	-0 48
Iron	+0 09	Copper (ic)	-0 52
Lead	-0 01	Silver	-0 97
Tin	-0 01	Mercury	-0 98
Arsenic	-0 40		

Zinc, cadmium, and iron have higher e m f 's than lead, and therefore would tend to dissolve and not be deposited from the electrolyte, while As, Sb, Bi, Cu, Ag, and Hg, having lower electromotive forces than lead, would tend to remain insoluble and go into the anode slime, tin, having the same e m f as lead, would dissolve and be deposited with the lead. This has been found to be the case in practice.

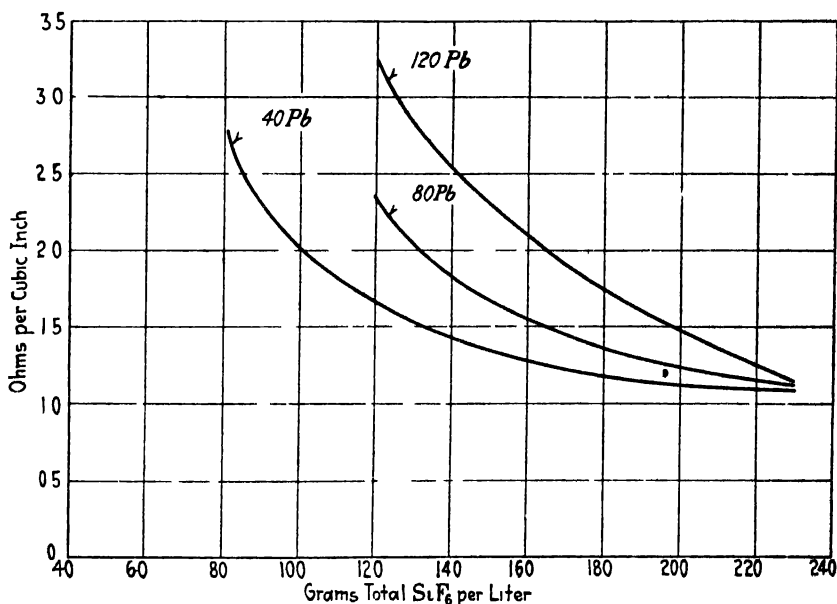


FIG. 1 — Electrolyte resistance curves

An anode of composite metals is not a mixture of metals from which one or more metals may be dissolved, leaving the other metals in the pure state, but a mixture of different compounds of the metals. Hence, there is not the full difference in e m f between lead and the other metals, as is shown by the above table. The e m f of solution of a lead-antimony alloy, for example, is nearer zero than that of pure antimony, but is sufficiently below that of lead to effect a separation.

**Conductivity of Electrolytes.**—Fused electrolytes have been proposed for the refining of lead. Borchers,<sup>2</sup> suggested a fused mixture of lead chloride and lead oxychloride in cells arranged with a series of grooves over which the molten crude

<sup>1</sup> *Loc. cit.*, "Lead Refining by Electrolysis."

<sup>2</sup> "Electrometallurgy," 1st Eng. ed., p. 338.



lead was allowed to flow as the anode. The cathode was made of iron and the collected lead ran down the cathode to a separate collecting space. Ashcroft<sup>1</sup> proposed to make molten lead in a pot the anode, and to rotate a metal cathode in the fused electrolyte, above the surface of the anode. He claimed the deposited lead would be suspended by the action of the magnetic field, instead of dropping back into the anode metal. No commercial applications of these processes are known.

Betts found that, within limits, an increase of lead content had little effect upon the resistance of fluosilicate electrolytes; increased acid content and increased temperature both decrease the resistance. Curves No. 1, 2, and 3 (Fig. 1), are plotted from his work. This figure gives the resistance in ohms per cubic inch for electrolytes containing 40, 80 and 120 g. of lead per liter, with varying content of  $\text{H}_2\text{SiF}_6$ .

**Impurities in Electrolyte.**—The only metals which tend to accumulate in the electrolyte are iron, zinc, nickel, and cobalt. Fortunately, these metals are not present in lead bullion to any great extent, or, if present, they can be eliminated readily by a simple dressing operation before the bullion is cast as anodes. Operating experience over a number of years has demonstrated that there is no tendency for injurious impurities to collect in the electrolyte, hence no electrolyte purification system has been found necessary.

**Acid Loss.**—The acid loss in electrolytic refining of lead varies from 15 to 30 lb. of  $\text{H}_2\text{SiF}_6$  per ton of lead. This loss is caused in part by the decomposition of  $\text{H}_2\text{SiF}_6$  at the anode, which may amount to as much as 2 to 3 lb. per ton of lead; partly by volatilization of  $\text{H}_2\text{SiF}_6$  in the evaporation of wash waters; partly by leaks in the tanks and circulation system; partly by drippage in removing the anodes and cathodes from the tanks; and by the acid retained in the anode slime as a result of imperfect washing. The last item, under normal operating conditions, causes the heaviest loss of acid, it often being found more economical to allow a small amount of soluble lead and acid to remain in the slime rather than to use an excessive amount of wash water, which must then be evaporated.

**Manufacture of Electrolyte.**—The first step in the manufacture of the fluosilicate electrolyte is the production of hydrofluoric acid. Ground high-grade fluor spar and 66° B $\phi$ . sulphuric acid are mixed in the approximate proportions of  $2\frac{1}{2}$  lb. of fluor spar to 3 lb. of acid, placed in a cast-iron or cast-steel retort, and heated gently at the start of the operation to prevent foaming of the charge. As the reaction proceeds, the temperature of the retort is gradually increased. The hydrofluoric acid passes to condensers as a gas and is absorbed by water in the condensers.

The hydrofluoric acid is next converted into hydrofluosilicic acid. This was formerly done in lead-lined or wooden tanks equipped with mechanical agitators, in which the hydrofluoric acid and pure silica sand were stirred until the reaction had been completed. This method has now been superseded by the Knorr<sup>2</sup> percolation system. Knorr used a series of two or three deep lead tanks arranged in cascade and filled with pure silica sand. Each tank was equipped with a water-cooled coil placed at or near the bottom in order to control the temperature. The hydrofluoric acid was fed slowly to the bottom of the first tank and allowed to percolate up through the bed of silica; overflowing the top of the first tank, the acid passed to the bottom of the

<sup>1</sup> *Electrochem. Met. Ind.*, 4, 357.

<sup>2</sup> Personal notes, Aug. E. Knorr.

second tank to percolate up through the second bed of silica; and then through the third tank in the same manner. The acid leaving the last tank carried only traces of free HF.

The hydrofluosilicic acid can be converted into lead fluosilicate by either of two methods. The first method consists in the electrolysis of the acid with lead anodes and cathodes separated by a diaphragm. Approximately 1.25 volts are required per cell. The anodes dissolve evenly and only a small amount of black spongy lead is deposited on the cathodes. The electrolyte produced by this method is clean and gives a good deposit at the start of the regular electrolysis. The second method of preparation of lead fluosilicate is to add the required amount of lead to the hydrofluosilicic acid in the form of white lead or basic lead carbonate. The lead content of the electrolyte is increased in the ordinary refining operations by allowing the regular electrolyte to drip through a tank or tower filled with shot lead, air is generally forced through the shot lead to assist in converting the lead to a soluble form.  $\text{H}_2\text{SiF}_6$  is added, when necessary, to maintain the desired acidity. In lead refining the tendency is to plate lead out of the electrolyte, the reverse is true of copper refining.

**Anodes.**—The lead bullion for refining is cast in the form of anodes, a pair of lugs being generally cast as part of the anode. These lugs serve to support the anodes in the electrolytic tanks and one of the lugs rests on the bus bar or triangle bar, thereby making the electrical contact. Cast iron is the material used in the construction of the anode molds. Both open and closed types of molds have been used. The anodes used at the plant of the U. S. Smelting Lead Refinery, Inc., at East Chicago, Ind., are 24 by 36 in. and about 1.25 in. thick at the top and 1.125 in. thick at the bottom. They weigh approximately 460 lb. each. The anodes at the Trail, B. C., plant of the Consolidated Mining & Smelting Co. of Canada are about 26 by 34.5 in. and taper from 1.25 in. at the top to 1 in. at the bottom in thickness, and weigh slightly more than 380 lb. each.

**Cathodes.**—Thin sheets of pure lead, slightly larger than the anodes, hung from copper cross-rods are used as the cathodes. These sheets are made by pouring molten lead over an inclined cast-iron plate of the proper size and shape. As the molten lead flows over the plate, the lead solidifies in a thin, even sheet, the excess molten lead flowing over the sides and bottom of the plate. These sheets, which weigh from 10 to 15 lb. each, are folded over a copper cross-rod and are fastened by punching or electric spot welding. The lead cathodes are very flimsy and must be straightened before being placed in the electrolytic tanks.

**Electrolytic Tanks.**—Wooden tanks, lined with  $\frac{1}{4}$  in. of an asphalt mixture, have given the most satisfactory service. The asphalt lining should be somewhat elastic to withstand shocks and temperature changes, and should still have a softening point sufficiently above the operating temperature of the electrolyte in order to prevent the lining from floating loose. The tanks are supported on timber frames, brick, or concrete piers. Heavy glass plates on the top of the supports give the necessary insulation.

Two systems of tank arrangement have been used: the cascade, and the Walker systems. The Trail plant uses the cascade system in double rows of five, six, and eleven tanks, while the East Chicago plant uses the Walker system of four tanks to a section. The Walker system permits of a considerable saving in bus-bar copper as compared with the cascade system, as copper triangle bars of small cross-section are used to conduct the current from the cathode cross rods of one tank to the anodes of the next tank. Bus bars are used only at the ends of the sections.

**Electrolyte Circulation.**—At Trail, the electrolyte enters the top tank in each cascade and flows in turn through each tank of the cascade to the collecting launders, thence to the pumps, which lift it to the gravity feed tank for distribution to the cells. At East Chicago the electrolyte passes through the four tanks of a section to the launders, is then pumped to a cooling tank, and is finally returned to the cells. The temperature of the electrolyte is held at 38 to 40°C. The rate of circulation is from 2½ to 4 gal. of electrolyte to each set of tanks per minute. The return launders are usually made of wood, asphalt lined; wood stave pipe has been proved to give good service. Bronze or copper centrifugal pumps and copper pump lines withstand the action of the electrolyte satisfactorily. The feed lines are made of hard-rubber pipe and the connections between tanks are of both hard and soft rubber.

**Tank Management.**—The tank-house crane lifts a tank load of anodes from a storage rack and lowers them into a tank in such a manner that one set of anode lugs rests on the positive bus bar or triangle of the tank, while the other set of lugs rests on a wooden bearing strip on the opposite side of the tank. The cathodes or starting sheets are then placed in the tank by hand, the cathode cross-rods making contact with the negative bus bar or triangle of the tank, but not touching the anode bus bar or triangle at the positive side of the tank. When a section has been completed, the current is turned on by unbolting and removing a bus-bar shunt.

The anodes usually remain in the tanks from 4 to 11 days, while the cathodes are removed at the end of 4 to 6 days and new starting sheets are placed in the tanks to receive the deposit for the balance of the time. The scrap anodes removed from the tanks amount to from 18 to 25 per cent of the weight of the anodes.

At the end of the refining period the cut-out shunt is bolted across the bus bars and the crane lifts a full load of cathodes from the tanks and carries them to a wash tank. The anodes are then removed as one crane load and placed in the anode washing tanks or machines. The electrolyte is siphoned from the tank and the slime is removed from the bottom of the tank. The tank is then ready for loading.

The cathodes are washed with a fine spray of warm water to remove the electrolyte and any slime which may adhere to them. The clean cathodes are then stacked in piles, the cross-rods are removed, and they are charged to the refined lead kettle for melting and casting as refined lead.

The greater proportion of the slime formed during the refining operation adheres to the scrap anodes and is removed with them from the tanks. This slime is removed in the wash tanks by the scrap washers. This was formerly done by men using scrapers and brushes, but it is now done by a machine equipped with revolving brushes. The washed scrap anodes are melted in cast-steel kettles and cast as anodes.

**Current Efficiency.**—The current efficiency will average about 90 per cent of the theoretical figure, though higher efficiencies have been obtained over short periods. The voltage per tank will average about 0.40 with a current density of 16 amp. per square foot of cathode surface, the anodes being spaced 4¾ in. center to center, and with an electrolyte at 40°C. carrying 6 per cent lead and 8 per cent free  $H_2SiF_6$ . The voltage gradually increases from 0.35 at the start to 0.44 at the end of the anode life. This is probably due to the increasing resistance of the slime blanket on the anodes. The lead deposited per kilowatt-hour will vary from 18.3 to 21.0 lb., depending upon the current efficiency and the resistance.

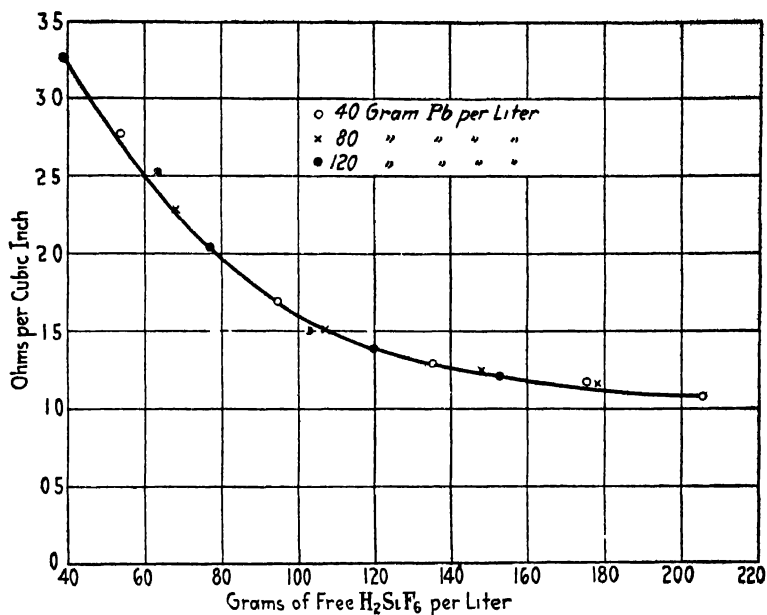


FIG. 2 — Ohms per cu. in. of electrolyte varying the free  $\text{H}_2\text{SiF}_6$  with 40, 60 and 80 grams of lead per liter

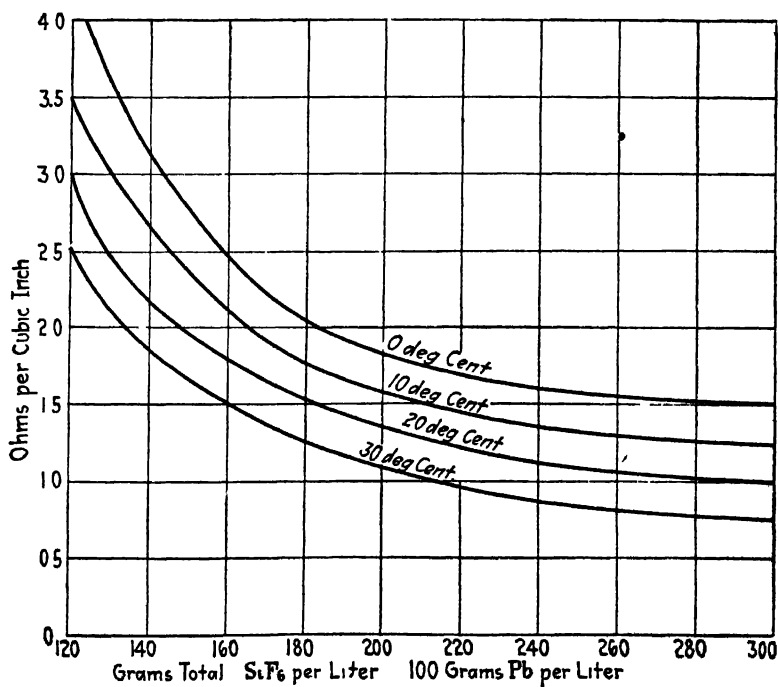


FIG. 3.—Temperature-resistance curves, fluosilicate electrolyte

**Slime Treatment.**—The anode slime is collected and pumped to a bronze or copper filter press where the excess electrolyte is removed. The slime is washed with weak wash liquors and with warm water until reasonably free of soluble lead. It is then treated with steam in the filter and blown with compressed air to reduce the moisture retained by the cake to as low a percentage as possible. The moisture in the discharged filter cake will average about 40 to 45 per cent, and, as this is too much moisture for furnace treatment of the slime, the moisture is reduced to about 5 to 10 per cent by a drying operation. One method of drying the slime is to load the filter cake into steel pans carried on cars, and place these cars in a chamber heated by gases from a fire box or by hot flue gases from the slime furnaces. The slime is often dried and allowed to oxidize in the flue.

The strong liquors and wash waters from the filter press are returned to the electrolyte and the weak wash waters are used to wash the next lot of slime. Any excessive wash water has to be evaporated before returning to the electrolyte. Proper planning and operation should permit the utilization of all the wash water without evaporation.

The dried slime is melted in a basic-lined reverberatory furnace to a slag and a metal. The slag contains the greater part of the Pb, Sb, and As, and only very small proportions of the Ag, Au, Cu, Te, and Bi carried by the slime; it is tapped from the furnace. The metal remaining in the furnace still contains some Pb, Sb, and As; these are slagged by a carefully controlled oxidation, leaving a metal composed of Ag, Au, Cu, Te, and Bi, with only traces of Pb and Sb. This metal is usually transferred to a second reverberatory furnace, in which the Bi, Cu, and Te are oxidized and removed as an oxide slag; the gold-silver alloy remaining in the furnace is refined by air and niter to doré and is cast in the form of plates suitable for parting.

The lead-antimony slags are retreated in a residue or desilverizing furnace to remove the small amounts of Au, Ag, Cu, Te, and Bi contained, and the desilverized slag is sent to the blast furnace for reduction to antimonial lead. The bismuth-copper-tellurium slags are retreated for the recovery of the bismuth, copper, and other metals of value.

The furnace treatment of anode slime volatilizes considerable arsenic, antimony, and lead, together with small amounts of the other metals in the slime. Some method for the collection of this fumed material is necessary. Wet scrubbers, bag houses, and Cottrell precipitators have been tried, but the best results have been obtained with the bag houses and Cottrells. The recovered fume or dust is retreated in the desilverizing furnace, yielding a desilverized lead-antimony slag, and a metal carrying the Cu, Bi, Te, Ag, and Au. This metal from the desilverizing furnace is reworked in the slimes-melting furnace, with slime charges.

**Wet Methods for Slime Treatment.**—A large number of wet methods have been suggested for the treatment of lead anode slime, but most of them have proved to be of little commercial value. McNab,<sup>1</sup> at the Trail plant, treated the press slime with caustic soda to neutralize any free acid remaining in the slime, with sulphur and a solution of sodium sulphide, or spent liquor from the antimony cells. This treatment extracts approximately 80 per cent of the antimony in the slime and only a small proportion of the arsenic. The sulphide solution, containing about 3.5 per cent of antimony, was siphoned off to a storage tank and passed through a series of antimony depositing cells. These cells were made of steel, with sheet-steel cathodes, and used regular lead refinery anodes. Ten cells were arranged in two cascades of five cells each; each cell had about 240

<sup>1</sup> "Lead Refining by Electrolysis," p. 323.

sq. ft. of both anode and cathode surface, and carried a current of 3,000 to 3,500 amp. with a potential of 1.5 volts. The maximum current efficiency (45 per cent) was obtained with an electrolyte temperature of 60°C. The solution, when leaving the last cell of the cascades, contained about 1 per cent of antimony and was returned to the slime-treatment tank for leaching more slime. Heavy losses of sodium sulphide were encountered, due to the oxidation of the sodium sulphide to sodium thiosulphate in the cells. This loss of sodium sulphide amounted to as much as 30 lb. per ton of lead bullion treated.

The lead anodes were used for about 10 days and then had to be renewed because of the heavy coating of sulphides on them. The cathode deposit was allowed to grow to a thickness of about  $\frac{1}{4}$  in., and was removed from one cathode at a time by hammering the steel cathode; the cathode deposit was washed, melted under an alkaline slag to remove arsenic, and cast as antimony bars. The antimony still contained some arsenic, and small amounts of gold and silver.

The slime from which the antimony had been extracted was dried, roasted at a low temperature, and leached with dilute sulphuric acid for the removal of the copper and some of the silver. The silver was precipitated on metallic copper, and the copper recovered as the sulphate by crystallization. The residue from the sulphate leach was melted in a basic-lined reverberatory furnace, using silica as a flux, the gold and silver eventually being recovered as a doré suitable for parting with sulphuric acid. This process proved to be uneconomical and was discontinued in favor of the direct smelting of the anode slime.

**Ferric Sulphate Treatment.**—Several methods of slime treatment have been proposed, in which solutions of ferric sulphate were to be employed. Ferric sulphate solutions react with slime very readily; metallic copper and cuprous sulphide are converted to copper sulphate; metallic antimony to hydrated trioxide of antimony; arsenic to arsenic acid; bismuth to basic bismuth sulphate; finely divided lead to lead sulphate; and, if the reaction is carried on at or near the boiling point of water, silver is converted to silver sulphate. The complete conversion of silver to silver sulphate is difficult because of the reducing action of the ferrous sulphate formed in the reaction. To dissolve approximately one-half to one-third of the silver requires a great excess of ferric sulphate; it is, therefore, much simpler to use only sufficient ferric sulphate to oxidize the other metals, leaving the silver insoluble. The chief difficulty of this method is the regeneration of the ferric sulphate solutions.

**Sulphuric Acid Treatment.**—E. F. Kern<sup>1</sup> proposed to roast a mixture of slime and sulphuric acid and to leach the roasted product with water for the removal of Cu, Bi, some of the Ag, and As. If sufficient sulphuric acid was used, the sulphates of Cu, Ag, Bi, and Sb were formed in the roasting operation; the antimony sulphate decomposed and became insoluble upon contact with water in the leaching operation. The antimony was to be extracted from the leached residuc by means of hydrofluoric acid, and was subsequently to be recovered by the electrolysis of the fluoride solution. The final residue was to be smelted and refined to doré.

F. C. Ryan<sup>2</sup> proposed to mix washed anode slime with sodium carbonate and to subject the mixture to a low-temperature roast, followed by a hot-water leach to remove As, Se, and S. The leached residue was then mixed with a quantity of 66°Bé.

<sup>1</sup> E. F. Kern, U. S. patent, 803601.

<sup>2</sup> Private notes.

sulphuric acid equivalent to the weight of the slime used, and was reroasted at a moderate heat until a definite color change had taken place. This color, which indicated the end point of the roasting operation, was a purplish gray and the color change was very sharp. The roasting temperature was just below the temperature at which sulphuric acid fumes became heavy. The roasted mass was then leached with water for the removal of copper and some of the silver. The silver was precipitated from solution as the chloride with a solution of common salt, and the copper was recovered from the clear liquor by precipitation on scrap iron. The silver chloride was washed and reduced to metallic silver by the action of metallic zinc or iron and dilute hydrochloric acid, was melted, and then cast as fine silver. The fine silver produced by this process always carried some As, Se, and Te, and had to be given a refining. The residue from the sulphate leach was washed and leached with hydrofluoric acid for the extraction of the antimony, the antimony being recovered by the electrolysis of the fluoride solution. The final residue was reduced to a doré for parting in a basic-lined reverberatory furnace. This process proved to be costly; it required the handling of large volumes of solution in order to keep the relatively insoluble silver sulphate in solution, and gave a final residue containing silver, gold, and lead sulphate, which is difficult to reduce to a doré suitable for parting. This last objection is common to all processes in which the lead is converted to the sulphate form.

**The Betts Process.**—The Betts process is the only electrolytic process used for the commercial refining of lead bullion. It has been used at four plants: Consolidated Smelting & Refining Co., Ltd., Trail, B. C.; U. S. Smelting Lead Refinery Inc., East Chicago, Ind.; American Smelting & Refining Co., Omaha, Neb.; an English Company (no data available), Newcastle-on-Tyne. The process has been in operation since 1902, producing the highest grade of refined lead from lead bullions which do not yield good results when treated by the Parkes process. The Betts process is particularly adapted for the refining of bismuth-bearing bullions. The Betts process cannot compete with the Parkes process in the refining of lead bullion such as that produced from Missouri and Oklahoma ores, except where extremely low power rates and very high fuel costs prevail.

**Metallurgical Data.**—The following data<sup>1</sup> represent the average of 15 months' continuous operation at the East Chicago, Ind., plant.

Weight of bullion treated per month. . . .	2,051 89 tons
Weight of cathode deposit per month. . . .	1,964 13 tons
Weight of scrap anode remelted . . . .	402 10 tons
Per cent of anode as scrap . . . . .	19 65 per cent
Weight of by-product lead to anode kettle. . . .	37.91 tons <sup>2</sup>
Weight of dry slime produced . . . . .	93 24 tons
Average current at switchboard . . . .	1,235 amp.
Average voltage at switchboard (161 tanks in series)	72 volts
Average pounds of lead per kilowatt-hour	18 1 lb.
Average number of tanks in circuit . .	161

<sup>1</sup> Personal notes

<sup>2</sup> The by-product lead came from the blast-furnace smelting of by-products and carried heavy silver and bismuth values. It was not fed to the anode kettle at a uniform rate, hence the silver and bismuth in the slimes do not agree with the silver and bismuth in the bullion. No assays of this material are available.

## ASSAY OF BULLION TREATED

	Average	Maximum	Minimum
Lead, per cent	97 60	97 83	97 33
Silver, ounces per ton	143 23	167 40	119 30
Gold, ounces per ton	1 635	2 010	1 230
Bismuth, per cent	0 291	0 370	0 219
Copper, per cent	0 055	0 070	0 039
Arsenic, per cent	0 352	0 680	0 140
Antimony, per cent	1 089	1 250	0 760
Tellurium, per cent	0 023	0 029	0 009

## ASSAY OF REFINED LEAD

	Average	Maximum	Minimum
Lead, per cent (difference)	99 98	99 99	99 97
Silver, ounces per ton	0 36	0 62	0 21
Gold, ounces per ton	Trace	Trace	Trace
Bismuth, per cent	0 0019	0 0040	0 0019
Copper, per cent	0 0025	0 0027	0 0019
Arsenic, per cent	0 0014	0 0022	0 0012
Antimony, per cent	0 0009	0 0019	Trace
Tellurium, per cent	None	None	None
Iron, per cent	0 0022	0 0040	0 0020
Tin, per cent	0 0040	0 0052	0 0016

## ASSAY OF SLIM

	Average	Maximum	Minimum
Silver, ounces per ton	3,608 50	4,669 40	2 748 00
Gold, ounces per ton	40 32	51 79	32 71
Lead, per cent	17 87	21 60	12 19
Bismuth, per cent	9 98	20 34	5 33
Copper, per cent	1 33	1 80	1 03
Arsenic, per cent	7 25	15 65	3 95
Antimony, per cent	28 03	33 00	24 24
Tellurium, per cent	0 78	1 39	0 44

The electrolyte carried approximately 4.5 per cent lead and 5 per cent free hydrofluosilicic acid during this period, and the average temperature was 37°C.



## CHAPTER XXXII

### THE ELECTROLYTIC ZINC PROCESS

BY FREDERICK LAIST<sup>1</sup> AND RUSSEL B. CAPLES<sup>2</sup>

**Definition.**—The method of producing zinc by the electrolysis of solutions of its salts is usually referred to as the “electrolytic-zinc process,” to distinguish it from the older pyrometallurgical operation usually referred to as the “retort process.” There are many variations in the application of the electrolytic process, both as to the zinc salt to be electrolyzed and as to the method of preparing the solution, but the only successful large-scale applications of the process up to the present time have employed dilute sulphuric acid leaching and electrolysis of the resulting zinc sulphate solution. These applications are cyclic processes in that they use the regenerated acid in the spent electrolyte as the source of sulphuric acid for leaching additional ore. Processes using zinc chloride solutions and some proposing to electrolyze fused zinc chloride have been tried out on semicommercial scales, but, with one possible exception, none has been made a commercial success.

**History.**—It has been known for more than fifty years that zinc could be deposited from its solutions by electrolysis, but no attempt was made to apply this knowledge on a large scale as a method for producing zinc from its ores until about 1880. Processes employing both zinc chloride and zinc sulphate solutions were tried from time to time without marked commercial success until about 1914, when the Anaconda Copper Mining Co. at Anaconda, Mont., and the Consolidated Mining & Smelting Co. at Trail, B. C., began independent investigations of the process as a means of solving the problem of treatment of complex ores occurring in their respective districts. Both were sufficiently successful to justify the erection of small test plants, which were rapidly enlarged as the war demand for high-grade zinc developed. Later, the Australian zinc producers were attracted by the successes of these companies and, after a thorough investigation of the process and of the results obtained, have built a plant at Hobart, Tasmania, for the treatment of concentrate from the Broken Hill mines.

The plant of the Anaconda Copper Mining Co. at Anaconda was more of a pilot plant for the development of the process than a commercial unit, but before dismantlement was producing more than 25 tons of zinc per day. A plant having a capacity of 100 tons of zinc per day was constructed at Great Falls, Mont., near the source of power, in 1916, and shortly after this plant started operations the plant at Anaconda was shut down and dismantled. The capacity of the Great Falls plant has been steadily increased until it is now capable of producing 300 tons of slab zinc per day.

The plant of the Consolidated Mining & Smelting Co. at Trail has been enlarged until it now has a capacity of nearly 200 tons of zinc per day, and may be further

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<sup>2</sup> Assistant general superintendent, Great Falls Reduction Department, Anaconda Copper Mining Co., Great Falls, Mont.

enlarged in the near future. A new concentrator for the treatment of ore from the famous Sullivan mine has just been completed and can supply sufficient concentrate for more than the present capacity of the electrolytic plant.

The Electrolytic Zinc Co. of Australasia, whose plant is at Hobart, Tasmania, first leased and operated the small test plant at Bully Hill, Cal., using concentrate shipped from its mines in Australia. Later, a pilot plant was built and operated at Hobart, and at the same time construction was begun on its present plant, having a capacity of about 150 tons of zinc per day.

These three plants produce practically all of the electrolytic zinc production of the world at the present time, and all employ sulphuric acid leaching followed by electrolysis of the resulting zinc sulphate solution, using a current density of about 30 amp. per square foot of cathode surface. There are, in addition to these, the plant of Brunner, Mond & Co., at Winnington, England, and some small plants in Japan and in Europe, about which little is known. During the war, many small plants came into existence, taking advantage of the high prices prevailing for grade A zinc, but none of these is now operating. The plant of Brunner, Mond & Co. is really a by-product plant, electrolyzing a zinc chloride solution, and has operated for about twenty-five years.

There is little doubt that the reason for the failures of the earlier plants using sulphuric acid leaching was the lack of appreciation of the very high degree of purity of solution required for successful electrolysis of zinc-sulphate solution. As soon as this fact was established and suitable methods of purification were developed, the success of the process was assured. Of course, many important details remained to be worked out and there is much yet to be done to perfect the process, but the fact that, with a sufficiently pure solution, zinc could be successfully deposited from an acid solution gave the process sufficient promise to justify the expense of working out methods of purification. There is now no doubt of the permanency of the process or of its superiority over the retort process for the treatment of most sulphide ores.<sup>1</sup>

**Application of the Process.**—The original idea in the development of the electrolytic-zinc process was to provide a method of treatment for the complex lead-zinc-silver ores, most of which contained some copper and iron and produced a concentrate low in zinc—30 to 40 per cent—and not well suited to the retort process. There is no doubt of the superiority of the electrolytic process for the treatment of this class of ores, due to higher recoveries of all of the metals and lower operating costs per pound of zinc, where power is available at a comparatively low rate. The concentrate originally treated at Anaconda and Great Falls contained less than 35 per cent zinc and about 15 per cent iron, and the concentrate now being treated at Trail, B. C. contains 40 to 45 per cent zinc and 18 to 20 per cent iron.

Improvements in concentration practice have made possible the separation of zinc and lead in many ores of this class, with the production of a much higher-grade zinc concentrate, containing less lead and silver, and the electrolytic process has proved to be successful in the treatment of the higher-grade concentrate. Experimental work on such concentrates as those produced in the Joplin district has shown that a high recovery of zinc can be obtained and the cost of production, per pound of zinc, is much less than for those concentrates which produce residues containing sufficient values in lead, copper, silver, and gold to pay the cost of treatment of the residue. With this class of concentrate, little residue is produced, and countercurrent

<sup>1</sup> For a more complete review of the history of the process, the reader is referred to RALSTON, OLIVER C., "Electrolytic Deposition of Hydrometallurgy of Zinc," McGraw-Hill Book Company, Inc., New York; HOFMAN, H. O., "Metallurgy of Zinc and Cadmium," McGraw-Hill Book Company, Inc., New York; and School Mines Met., Univ. Missouri, (Rolla, Mo.), *Bull.*, February, 1919.

washing may be substituted for filtration, and washing by repulping. Also, the absence of much copper, arsenic, and antimony greatly simplifies the problem of solution purification. All classes of sulphide ores can be made to yield higher recoveries of all of the metals contained with the electrolytic process than with the retort process, and it is only in especially favored localities that the treatment can be carried out more cheaply by the retort process. It is doubtful whether the retort process can successfully compete with the electrolytic process in any locality in the United States in the treatment of sulphide ores.

One essential requirement of the electrolytic process is a large source of power and, of course, the cheaper the better. Up to the present time, the large electrolytic zinc plants have been located in regions having large amounts of comparatively cheap water power. As power is the largest single item of the cost of the operation of an electrolytic-zinc plant, it is necessary to obtain the lowest rate possible, and the lower the rate the wider the range of ores that may be treated. It is not necessary in all cases that water power be available, because power can be generated from coal in some localities and transmitted to the source of ore supply, thereby saving the freight on

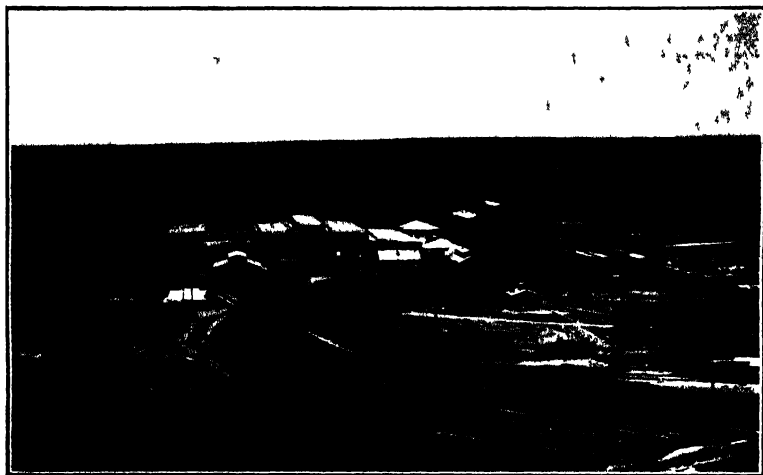


Fig 1—Great Falls Mont zinc plant

both ore and coal as a credit to the cost of producing power. The amount of coal and coke required by a retort plant using coal for fuel is just about sufficient to produce the power required for an electrolytic-zinc plant of equal capacity. Within reasonable distances, it is cheaper to generate the power required at the source of fuel, and transmit the power, than it is to ship the coal. Water power is in most cases cheaper than power generated from coal, but usually must be developed in large units. As the electrolytic process requires a large amount of power, some possible sources of water power, now undeveloped, due to lack of sufficient demand nearby, may eventually be developed for the location of electrolytic-zinc plants. The total power requirement in order for a plant to produce 100 tons of zinc per day is about 20,000 hp.

From the standpoint of labor requirement and working conditions, the electrolytic process is far superior to the retort process. For the production of 100 tons of zinc per day from a concentrate containing 55 per cent zinc, less than 200 men are required, and a high percentage of these are comparatively unskilled labor. The working conditions in an electrolytic plant compare favorably with the best of industrial plants and attract a high class of labor, making for a steady supply of labor of more than average efficiency.

The cost of construction of an electrolytic-zinc plant is necessarily high, due to the amounts of copper, lead, and aluminum required for bus-bar lines, electrodes, electrode-support bars, solution piping, acidproof pumps, and other acidproof equipment. The large installation of electrical equipment required is also a heavy item of expense. The comparatively high salvage value of an electrolytic plant offsets the heavy first cost. No more money need be spent for buildings for an electrolytic plant than for a retort plant, the difference in cost being largely for equipment contained in the buildings. Crediting the salvage value of an electrolytic plant over that of a retort plant, the ultimate difference in cost of plant will be little, if any, in favor of the retort plant.

Grade A zinc is the normal product of an electrolytic plant and commonly commands some premium over the lower grades. The iron content is less than 0.005 per cent and the lead content is usually less than 0.05 per cent, the cadmium content is controlled by the extent of the purification of solution prior to electrolysis. It is possible to produce zinc of any specified analysis, varying either the lead or cadmium content to suit the customer. This is a natural selling advantage for the electrolytic plant and is certain to affect the disposal of ordinary "Prime Western" as the production of electrolytic zinc increases.

The high recovery of metals other than zinc by the electrolytic process, and the comparatively small amount of residue produced, will, in some cases, result in the production of residue of sufficient value to pay the cost of treatment, while, if the retort process had been employed, a residue of no value would have been produced. A high recovery of lead from electrolytic-plant residue may be obtained by brine leaching, and at a moderate cost as the residue requires no further preparation for brine leaching. With some ores, the credit from residue may amount to a large item in favor of the electrolytic process.

Combinations of circumstances are possible that will eliminate either the electrolytic or the retort process from consideration for the treatment of the ores from any given locality, but the development of the electrolytic process has progressed to a point where it must be seriously considered and should be thoroughly investigated before finally adopting a method of treatment for any class of ores in any locality.

The large amount of soluble silica in carbonate and silicate ores is decidedly detrimental to the electrolytic process, making the separation of residue and solution a difficult problem. Not a great deal of experimental work has been done on this class of ores with the electrolytic process, but after the process has been successfully applied to other classes of ores it is probable that some method of handling the oxidized ores will be worked out. It is only natural that, with the difficulties encountered in the treatment of sulphide ores, any other class of ores presenting additional problems should be left alone until the simpler problems have been successfully solved. Great progress has been made in handling soluble silica in connection with the treatment of sulphide ores, and there is no reason to believe that larger quantities of soluble silica will not eventually be suitably controlled to permit of the application of the electrolytic process to the silicate and carbonate ores.

The electrolytic-zinc process is particularly suited to the treatment of concentrate produced by the flotation process, as finely ground calcine is essential to successful leaching, and the smaller the size of the particle to be roasted the lower the temperature necessary completely to eliminate its sulphur content. A constantly increasing percentage of zinc concentrate produced is flotation concentrate, especially since the quite general application of selective flotation to ores containing both zinc and lead.

**Outline of Process.**—A broad division of the process groups the necessary operations under three headings: (1) preparation of ore or concentrate for leaching; (2) treatment of roasted ore or concentrate to produce a pure solution of the

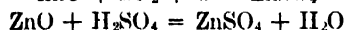
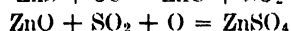
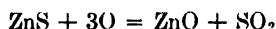
zinc salt to be electrolyzed; (3) electrolysis of the pure solution to produce metallic zinc and to regenerate the leaching solution.

**Preparation of Concentrate for Leaching.**—For concentrate containing zinc sulphide, this step comprises roasting to convert zinc sulphide into zinc oxide or zinc sulphate as the essential result. The conditions under which roasting is carried on also control to some extent the solubility of iron, copper, and silver in the leaching solution. Roasting is primarily the most important step in the process, as the possible recovery of zinc is entirely dependent upon the degree of perfection of the roast, when dilute sulphuric acid leaching is employed. Other methods than roasting may be employed, but are not commercially feasible at the present time under ordinary conditions.

**Production of a Pure Zinc Solution.**—Préparation of pure zinc sulphate solution and leaching with dilute sulphuric acid (10 to 15 per cent) is the only successful application of the process so far developed and is the only application to be described fully. Not only zinc, but many other metals, if present in the concentrate, are dissolved by dilute sulphuric acid, and most of the metals other than zinc must be removed from solution to insure successful electrolysis. This division of the process is really a combination of several steps: leaching to dissolve zinc, separation of solution and insoluble residue, purification of solution, and clarification of solution. This is the second most important step in the process, as, given perfect roasting, the recovery of zinc is dependent upon proper leaching and filtration, and the electrolysis of zinc sulphate solution is dependent upon proper purification of solution.

**Electrolysis of Solution.**—The essential factor in the successful carrying out of this step is the purity of the solution to be electrolyzed. Probably no other process operating on a large scale requires the same degree of purity of solution as the electrolytic-zinc process. Other factors having more or less influence on this step are temperature of electrolyte, current density, ratio of zinc to acid in electrolyte, period of deposition, and purity of electrodes. Lead anodes and aluminum cathodes are used, and usually not more than 30 amp. per square foot of cathode surface. Neutral or slightly basic solution is fed to the cells and for each unit of zinc deposited approximately one and one-half units of acid are regenerated. All zinc in solution is not deposited—usually not more than 75 per cent—and the spent electrolyte, containing approximately 25 per cent of the zinc brought in in the cell feed and the acid regenerated by the deposition of 75 per cent of the zinc, is returned to the leaching division. The zinc deposit is removed at the end of regular periods and is melted and cast into slabs.

The simple chemical reactions involved are:



In addition to the divisions of the process outlined above, there might be added a fourth, treatment of residue. As the electrolytic-zinc process is particularly applicable to the complex ores of the western states, there is in nearly every instance sufficient value in the residue to require some method of treatment.

The great variety of ores to which the process is applicable, results in production of several classes of residue requiring more than one method of treatment to produce the

greatest possible return from each class. In some cases lead smelting is the best method of treatment; in others, copper smelting; in others, a wet method, and in some a combination of methods, is the most satisfactory treatment.

**Roasting.**—All electrolytic-zinc plants now operating are using a modified Wedge furnace. The most common type is 25 ft. in diameter inside the shell, with seven roasting hearths and a top hearth for drying the feed. A 5-ft. diameter, brick-covered, hollow, revolving center shaft carries twenty-six cast-iron, water- or air-cooled arms; four for each the drier and first hearths, and three for each of the remaining six hearths. The shaft is supported on a step bearing, and is revolved by a bevel pinion driven through a set of reducing gears. The speed may be varied from one revolution in  $1\frac{1}{2}$  min. to one revolution in 4 min. Water, or air, for cooling is delivered to the arms through a column revolving with the center shaft and connected to the main by a swivel joint. Fire boxes are placed on either the sixth or seventh hearths, usually two boxes to a furnace, spaced 180 deg. apart.

Concentrate is fed by an apron feeder, driven from the revolving center shaft, which discharges on the outer edge of the drier hearth. It is advanced across the drier hearth by means of rabbles or rakes fastened to the arms, and drops through holes on the inside of the hearth to the next hearth below, the first roasting hearth. Rakes on the arms on this hearth are set to move the material outward and, when it reaches the circumference of this hearth, it falls through drop holes onto the next hearth, and so on down through the furnace and into two steel hoppers provided for temporary storage for calcine. These hoppers discharge into conveyors or into cars for removing the calcine. At Trail, a conveyor made of lengths of cast-iron pipe with a screw-conveyor flight cast on the inside and mounted on rollers is used to carry calcine from the roasting furnaces to the leaching plant. The gases pass upward through the drop holes until the first roasting hearth is reached, where uptake flues lead to the main gas flue, or oftakes may be provided from more than one hearth, thereby giving better control of temperature on the different hearths without admitting too much excess air.

Roasting flotation concentrate in this type of furnace is productive of a large amount of flue dust, which must be collected and returned to the furnaces. At Great Falls, the old flue system built for copper-smelting operations is used and a very satisfactory clearance of gases is obtained. At Anaconda and at Trail, Cottrell treaters are used and give nearly perfect clearance.

The materials to be treated are flotation or fine table concentrate over 50 per cent of which will pass a 200-mesh screen—flue dust, and crushed calcine lumps. In order to keep down the amount of flue dust to be recirculated, the gas volume must be kept at a minimum by carefully regulating the door openings on each hearth to give only the amount of air necessary for roasting and for cooling the upper hearths. The gas leaving a furnace is saturated with dust particles of a given weight or less, the maximum weight depending upon the velocity of the gas. As the velocity increases, the weight of particles decreases much more rapidly and the total amount that can be carried decreases. By returning all flue dust to one furnace, or more if necessary, and cutting the gas volume on these furnaces as low as possible, the amount of dust recirculated is kept at a minimum.

The capacity of one of this type of furnace varies widely with the class of material being treated, being greater for complex, low-zinc concentrate than for higher-grade concentrate. The normal limits are from 35 to 45 dry tons of new feed per 24 hr. The limiting factor for tonnage of low-zinc, complex concentrate is the ability to cool the upper hearths without undue production of flue dust. In general, the higher the

zinc content of the concentrate the more slowly the roast progresses and the smaller the capacity of the furnace. In addition to the concentrate tonnages given, a furnace will roast its proportion of flue dust and crushed calcine lumps.

Lump coal, pulverized coal, and oil are the fuels commonly used, but probably the most satisfactory fuel would be gas. A large part of the ash from pulverized coal settles in the furnace and flue system and eventually finds its way out in the calcine, where it adds to all subsequent operating costs, such as leaching, filtration, and residue treatment. Fuel requirements vary with the class of concentrate being roasted, the observed limits being from 7 to 18 per cent of the weight of concentrate treated, when using pulverized coal containing heat value of 10,000 B.t.u. Oil requirements are about 20 per cent less than coal on a heat-unit basis of comparison.

**Object of Roasting.**—Zinc sulphide is practically insoluble in dilute sulphuric acid at ordinary leaching temperatures. Zinc oxide is readily soluble in dilute sulphuric acid, and zinc sulphate is water soluble. The object of roasting is, therefore, to convert zinc sulphide as completely as possible into zinc oxide and zinc sulphate. Only enough zinc sulphate to supply the acid requirements of the plant is normally desirable, as any excess must later be discarded as solution to avoid building up acid in the system and thereby increasing the zinc content of the solution. As the acid requirements of the process are small in amount, it is not desirable to form a high percentage of zinc sulphate, from 2 to 3 per cent sulphate sulphur in the calcine usually being sufficient. The only acid losses are as insoluble sulphates in the residue and solution losses, chiefly as solution entrained in the residue. The greater the ratio of residue to calcine the more impervious the residue is to wash water, and the higher the zinc content of the solution the greater the loss of soluble sulphates. The higher the lead and lime contents of calcine the greater the loss as insoluble sulphates. Some acid is also lost as basic iron sulphate.

**Ferrate.**—Zinc oxide and iron oxide combine under certain conditions to form zinc ferrate ( $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$ ) which is insoluble in warm, dilute sulphuric acid. This is the chief source of loss of zinc with the electrolytic process and can be prevented only by the careful control of roasting conditions, and then only imperfectly. No set of roasting conditions has yet been perfected whereby no ferrate is formed when iron is present in the concentrate. The formation of ferrate is dependent upon the iron content of the concentrate, the temperature of roasting, the association of zinc and iron, and the length of time of roasting. It is impossible accurately to predict the amount of ferrate which will be formed, from the analysis of the concentrate alone. Iron and lead sulphides roast at lower temperatures than zinc sulphide and it is possible to make a preferential roast by keeping the initial roasting temperature below  $600^\circ\text{C}.$ , and thereby reduce the formation of ferrate. If the initial temperature is too high and zinc and iron sulphides are roasting on the same hearth of the furnace, the intense heat surrounding particles of freshly formed  $\text{ZnO}$  and  $\text{Fe}_2\text{O}_3$  will effect their combination. If, however, the  $\text{Fe}_2\text{O}_3$  is formed first and the  $\text{ZnO}$  later, at a temperature of  $650^\circ\text{C}.$  or less, the chances of combination are greatly reduced. When the particles of zinc and iron sulphides are very intimately mixed, as in marmatite, preferential or selective roasting is nearly impossible and a high percentage of ferrate is bound to result. The only rule that can be given is to keep the temperature as low as possible throughout the furnace—a maximum of 600 to  $650^\circ\text{C}.$ —and, especially, to keep the tempera-

ture on the first two or three roasting hearths below 600°C. As the iron content increases, the possibility of making a selective roast increases. Low iron concentrate, such as that from Joplin district, roasts with complete combination of iron content with zinc as ferrate. Figure 2 gives data taken from practice for roasting a low-zinc, high-iron concentrate. The data given in Table 1 were

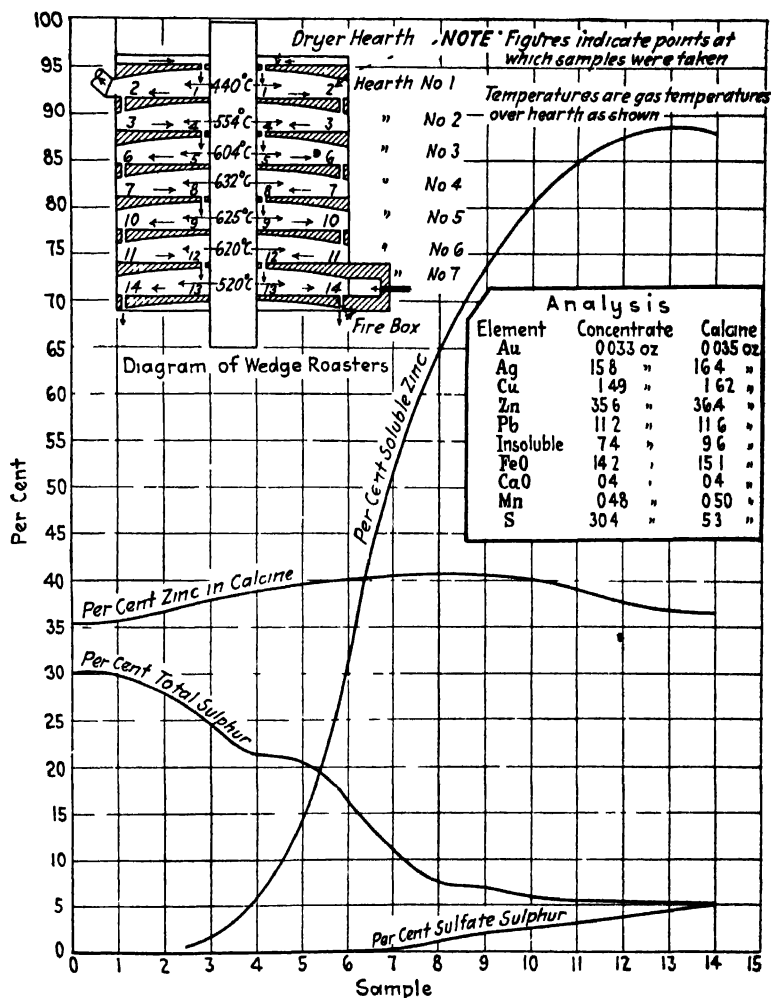


FIG. 2. Roasting low grade concentrates without returning flue dust

obtained in the laboratory on samples of complex concentrates from the same district and show that the analysis is not the all-controlling factor in ferrate formation, the sizes of particles and the intimacy of contact of particles being influencing factors



TABLE 1

	Per cent Zn	Per cent Pb	Per cent Fe	Per cent S	Per cent SO <sub>4</sub>	Per cent soluble Zn	Per cent As	Per cent Sb
Concentrate A	39.6	13.8	6.6	29.2			0.10	0.04
Calcine A	37.8		6.3	8.8	8.5	92.6	0.08	0.03
Concentrate B	47.3	3.4	7.0	32.2			0.53	0.17
Calcine B	44.8		6.6	8.5	8.1	94.2	0.23	0.05
Concentrate C	34.9	13.6	11.6	32.0			0.11	0.03
Calcine C	36.8		11.8	5.4	5.2	92.7	0.09	0.03
Concentrate D	34.3	17.8	7.5	28.4			0.08	0.03
Calcine D	33.8		7.4	6.0	5.9	89.1	0.07	0.03
Concentrate E	30.8	3.6	16.4	35.3			0.90	0.19
Calcine E	30.4		16.0	8.5	8.5	87.2	0.24	0.11

NOTE.—Roasts made at low temperature — 650°C. maximum with no attempt to control sulphate sulphur

**Roasting Temperature.**—The maximum temperatures in roasting for the electrolytic process may be given as approximately 650°C. for complex, low-zinc concentrate and 750°C. for high-grade concentrate. The initial temperatures should be well under 600°C. for at least one roasting hearth in treatment of either class of material. Lead sulphide fuses without roasting, if the initial temperature is too high, and forms a hard crust on the hearth under the rakes. It also coats particles of zinc oxide and forms lumps which pass through the furnace unroasted and must be screened out of the calcine, crushed, and returned to be reroasted. The temperature lower down in the furnace must be raised to complete the roasting of zinc sulphide and to prevent the formation of an excessive amount of zinc sulphate. If the temperature is raised too much, an excessive amount of ferrate will be formed. Each concentrate is a problem in itself and the best conditions must be determined experimentally. Figures 2 and 3 give temperatures from the operation of two furnaces on widely different classes of concentrate.

Temperature regulation is obtained by varying the admission of air into the furnace and by varying the amount of fuel used. Some heat is lost by radiation and some through the cooling of arms with water or air. The remainder is carried out in calcine and by the gas leaving the furnace. With the same zinc content, but varying the amount of lead sulphide and iron sulphide in the feed, very different heat problems will be presented. Analyses of two concentrates and the resulting calcines taken from monthly averages in actual practice are given on p. 1105:

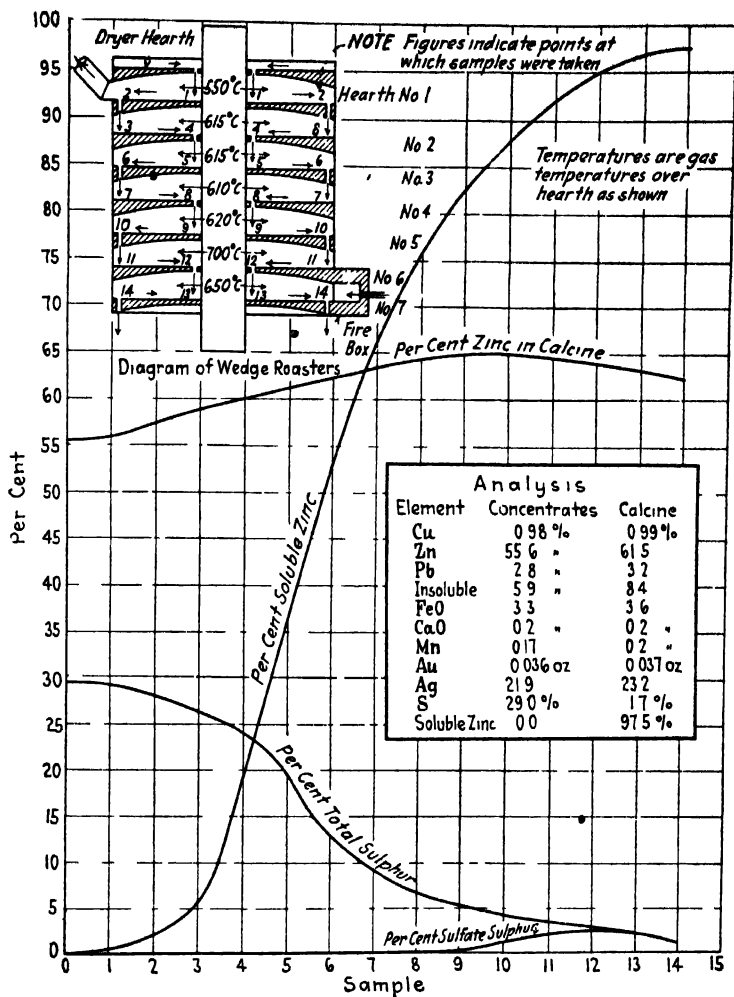


FIG. 3. Roasting high grade concentrates in Wedge furnace

TABLE 2

	Per cent Zn	Per cent Pb	Per cent Fe	Per cent S	Per cent SO <sub>4</sub> S	Per cent soluble Zn
Concentrate A	32.3	8.2	15.6	32.4		
Calcine A	35.0			3.8	3.2	80.3
Concentrate B	32.3	16.4	8.7	28.4		
Calcine B	34.6			3.9	3.5	88.5

The difference of 4 per cent in sulphur content of these concentrates is due to the difference in iron content and must be eliminated on the upper hearths, requiring much more cooling air for concentrate A. If the lower part of the furnace is required to do too much of the roasting, the larger volume of hot gases from the lower hearths tends to raise the temperature on the upper hearths and will require more cooling air on these hearths. It is essential to keep the volume of gas as low as possible on the lower hearths if proper control of upper hearth temperatures is to be obtained without too great a total gas volume. Table 3 gives the temperatures and SO<sub>2</sub> analyses, by volume, of the gas on the different hearths of a furnace roasting low-zinc concentrate with excellent results, using pulverized coal for fuel

TABLE 3

Hearth	Per cent SO <sub>2</sub>	Gas temperature, degrees Centigrade	Calaine temperature, degrees Centigrade	Per cent CO <sub>2</sub>
1	3 0	438	459	2 5
2	2 8	560	551	2 5
3	2 2	626	665	2 7
4	1 2	650	665	2 8
5	0 5	622	638	3 4
6	0 3	622	652	3 6
7	0 1	543	602	3 0

**Sulphate Roasting.**—The term "sulphate roasting," as commonly used in connection with roasting for electrolytic zinc, is really a misnomer, as it is not desirable to form more zinc sulphate in roasting than is required to offset the loss of acid in the leaching plant. The term was coined to apply to the set of roasting conditions necessary to supply acid for a plant using limestone or milk of lime for neutralization in the leaching division, thereby greatly increasing the loss of acid as insoluble sulphates in the residue. Unless sufficient acid was formed in roasting to offset this loss, fresh acid was added to the system. The maximum amount of sulphate sulphur formed in practice was about 6 per cent of the weight of calaine. Ordinary roasting practice on the same class of material would give about 3 per cent sulphate sulphur.

The method employed to increase the percentage of sulphate sulphur was to keep the temperature of the furnace below 600°C. and to admit sufficient air on the first three roasting hearths to keep the temperature below 550°C., thereby reducing the SO<sub>2</sub> content of the gas below 2 per cent on every hearth. At higher temperatures and with higher concentration of SO<sub>2</sub> less sulphate was formed. The presence of freshly formed oxides of iron also seems to aid the formation of sulphate. The reaction involved is undoubtedly  $\text{ZnO} + \text{SO}_2 + \text{O} = \text{ZnSO}_4$ , the iron oxide acting as a catalyzer. If the reaction were  $\text{ZnO} + \text{SO}_3 = \text{ZnSO}_4$  there should not be any free SO<sub>2</sub> present in the flue gases also carrying ZnO, but the gas leaving the roasting furnace actually does contain some free SO<sub>2</sub> and flue dust high in ZnO. Also it is known that some  $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$  may be decomposed, forming ZnSO<sub>4</sub>, by passing SO<sub>2</sub> gas over zinc-plant residue.

The only real difference between the so-called "sulphate roasting" and normal roasting is the lower temperature, especially on the lower hearths, and the greater amount of air admitted when "sulphate roasting." This gives an excessive production of flue dust, due to increased gas volume passing through the furnace. The only need for sulphate roasting is with concentrate or ore containing high percentages of lime, barium, or lead.

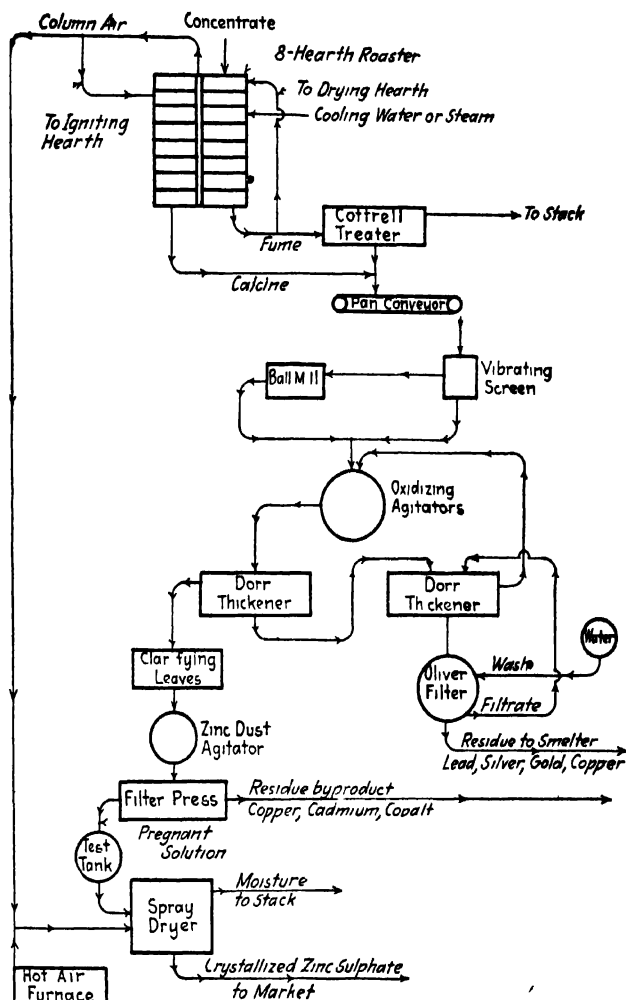


FIG 4 — Flow sheet of Coolbaugh sulphating process

Experiments are now being conducted in Colorado using the Coolbaugh process, in which a high percentage of zinc is converted to zinc sulphate. A down-draft roasting furnace is used, giving a much higher percentage of  $\text{SO}_2$  on the lower hearths than is obtained with the usual up-draft furnace. This method of roasting can hardly be said to be part of the electrolytic-zinc process, as its use is applicable to the process only under conditions where a market is available for comparatively high-priced

sulphuric acid produced from the spent electrolyte, or where zinc is so cheap that the spent electrolyte may be wasted.

Another process, which has been proposed as an alternative for roasting, proposes mixing concentrate with strong sulphuric acid and heating the mixture gradually to 650°C., thereby converting most of the zinc sulphide into zinc sulphate and decomposing iron and copper sulphates. All soluble silica is dehydrated, avoiding any trouble from gelatinous silica in the leaching division. The resulting calcine is leached with water and the spent electrolyte from the electrolysis of this solution is evaporated to supply the necessary strong acid for the decomposition of zinc sulphide. Mechanical difficulties have discouraged large-scale tests and it is unlikely that the process will ever become of commercial importance.

**Behavior of Impurities in Roasting.**—Varying percentages of arsenic and antimony are eliminated in roasting zinc concentrates, as is illustrated in Table 1, probably depending upon the form in which they occur in the concentrate. Fortunately, most zinc ores are quite low in these impurities, as they are among the most injurious to the process.

Some copper combines with iron in roasting, the combination being insoluble in dilute sulphuric acid. Concentrates containing high percentages of iron produce a less proportion of soluble copper than those low in iron. Some copper sulphate is formed on the upper hearths of the furnace, but this is decomposed by the higher temperature on the lower hearths.

If the temperature of the upper hearths is too high, a considerable percentage of the lead content of the concentrate is volatilized, and some of the lead sulphide fuses and works into the hearth bed, forming a hard crust.

One disadvantage of the sulphate roast is the high percentage of soluble iron in the calcine, indicating that some iron sulphate is also formed in roasting. In the usual roasting practice the finishing temperature is high enough to break up iron sulphate, and most of the iron present in the calcine is insoluble in dilute sulphuric acid. Too much soluble iron will render the residue from the leaching plant impervious to the passage of wash water, as all iron dissolved is finally precipitated from solution as ferric hydrate, or basic sulphate.

Less silver is rendered soluble in roasting at low temperatures than at higher temperatures but when the initial roasting temperature is too high some silver is volatilized.

Chlorine, if present, is largely eliminated during roasting, as most chlorides are volatile at the temperature of roasting.

**Notes on Roasting.**—The bedding of calcine between the rakes and the brick hearths is found to contain a high percentage of zinc sulphate, especially on the second, third, and fourth hearths. This material becomes quite hard, the hardness increasing with the temperature of roasting. At frequent intervals the rakes are removed from an arm, a plow is put on, and the shaft is revolved, cutting this crust loose, so that it may be removed through the furnace doors. If allowed to stand in the open, this crust will gradually absorb moisture and disintegrate. In order to avoid a too heavy formation of crusts, sand is put on the hearths over the brick before starting a new furnace, and is replaced about once in two years thereafter.

Some lumps are formed in roasting, even when temperature control is properly regulated, and should be removed before calcine is delivered to the leaching tanks. Also, calcine should be cooled to avoid injury to employees and to remove fire risk.

At Great Falls, the Anaconda calcine cooler is used and a  $\frac{1}{8}$ -in. trommel screen is fastened to the end of the cooler. The oversize from the  $\frac{1}{8}$ -in. trommel is delivered to a  $\frac{3}{8}$ -in. trommel, the undersize is ground and mixed with the  $\frac{1}{8}$ -in. trommel undersize, and the oversize from the  $\frac{3}{8}$ -in. trommel is crushed and returned to the roasting furnaces. It has been found that the larger lumps are so imperfectly roasted in the centers that re-roasting will pay, but lumps smaller than  $\frac{1}{4}$  in. or  $\frac{3}{8}$  in. contain insufficient sulphides to pay for re-roasting. At Park City, Utah, the Baker cooler is used. At Trail, an internal screw-conveyor system handles calcine from roasters to leaching tanks and no additional cooling is required.

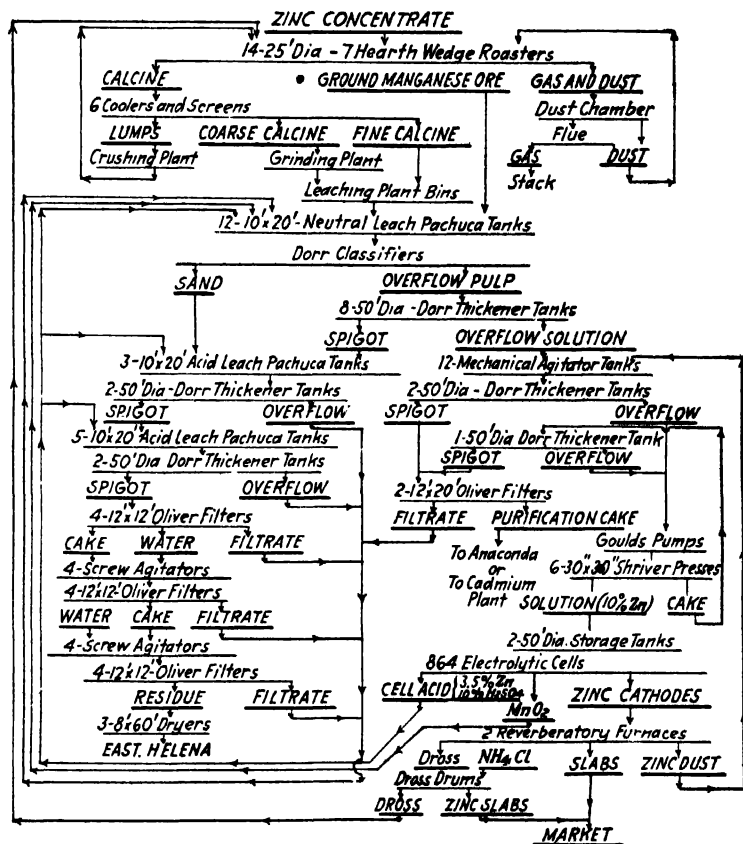


FIG. 5.—Flow sheet, Great Falls electrolytic zinc plant.

**Leaching and Purification.**—These operations are combined under one heading, as most of the purification of solution is accomplished in the leaching tanks. When a double leach is made, the first, or "neutral," leach is, in reality, more of a purification operation than it is a leaching operation.

**Equipment.**—Standard types of leaching, settling, filtration, and clarification equipment have been adapted to the needs of the process, thereby simplifying the mechanical problems. Pachuca tanks are used for leaching, the size depending upon the needs of the plant; standard thickeners are used for thickening of

pulp; standard continuous vacuum filters are employed for filtration of the thickened pulp; any type of mechanical agitator of large capacity will answer for zinc-dust purification, and standard pressure filters are used for clarification of solution. All equipment should be acid- and copperproof. Lead and wood are commonly employed for the construction of parts in contact with acid, and lead, copper, or bronze for parts in contact with neutral solutions containing some copper. Although this requires considerable extra capital outlay over the cost of similar equipment of iron or steel construction, the salvage or scrap value is a very high percentage of the first cost.

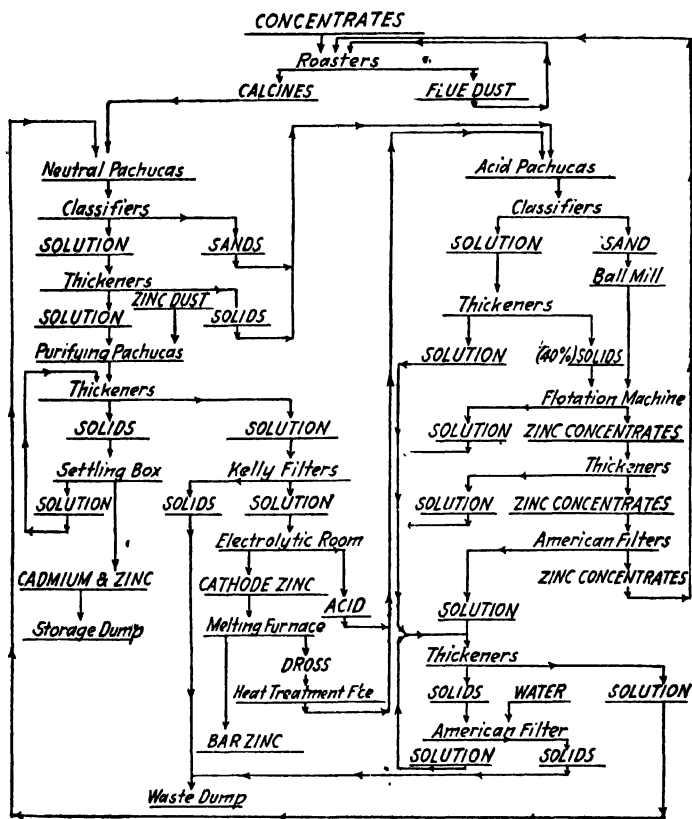
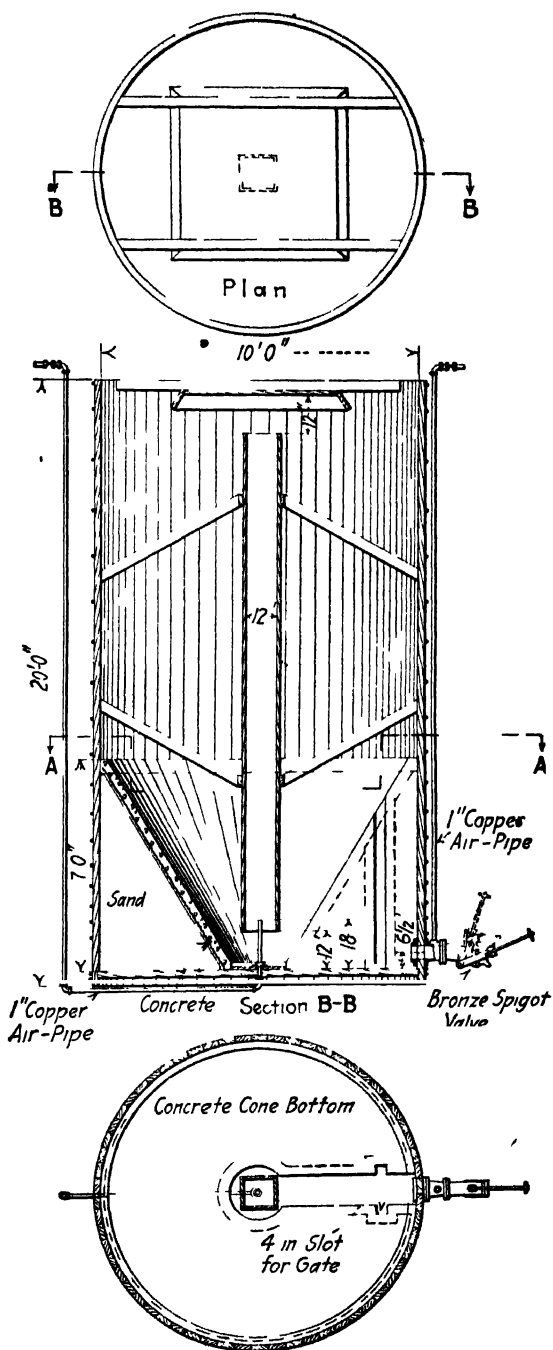


FIG. 6.—Flow sheet of Consolidated Mining & Smelting Co., Trail, B. C.

In the larger plants, continuous leaching has been adopted as standard practice, to which the Pachuca tank is especially well adapted. Figure 6 shows the method of supporting the center air lift and of admitting air into the lift. Air under 20 to 30 lb. pressure is commonly employed, the consumption varying from 100 to 150 cu. ft. free air per tank per minute to maintain sufficiently violent agitation to prevent classification of the pulp. The rate of flow of pulp through the series of tanks may be regulated by any means of partially closing the connection between tanks. The number of tanks in series depends upon the volume of pulp to be handled per unit of time and the length of time required to complete the reactions. The common size of



Section A-A

FIG 7—Pachuca leaching tank



tank employed is from 8 to 10 ft. in diameter and from 20 to 30 ft. deep, with an 8- or 10-ft. inverted cone built into the bottom to deflect solid particles to the center of the tank so that they will be drawn into the center air lift. The tank and air lift are made of wood and the tank staves are bound together with iron hoops covered with sheet lead. A lining of hard wood placed inside the tank at the elevation where the air-lift discharge strikes the side of the tank protects the tank staves from erosion and this lining may be renewed when worn through, thereby greatly lengthening the life of the tank proper. Each tank is provided with a bottom-discharge connection to facilitate cleaning.

Classifiers are used to separate any particles of heavy sand in the leached pulp before sending to the thickeners. This sand is ground and returned to the leaching system.

Standard thickeners are used for the separation of solution and solids. The arms should have more slope than is usually given in cyanide practice and a much larger discharge cone for thickened pulp should be provided, especially for thickeners handling an acid product. The tanks are made of wood staves held together with iron hoops covered with lead. Overflow launders are made of wood and are fastened to the inside of the tank.

All piping and fittings for the vacuum filters are made of copper and bronze. The drums or frames are of wood or bronze and the tanks are either of wood, or steel with lead lining. For filtration of slightly acid pulp, the best filter cover yet developed is a pure, unwashed wool blanket, with the nap on the outside of the filter. Such a cover will not "blind" easily, as the threads do not swell when soaked with dilute acid and the nap acts as an automatic valve, closing when under suction and opening and freeing the cloth when under pressure. The natural oil in the wool protects the fiber against the attack of dilute sulphuric acid. The dry-vacuum system is used, the solution receiver and moisture trap being made of wood. To prevent some vapor or spray from getting into the vacuum pumps and corroding valves and cylinders, receivers and traps should be of extra-large capacity and the traps should be placed much higher than the vacuum would normally indicate to be necessary.

Mechanical agitators with bronze or wood shafts and impellers are used for zinc-dust purification of solution. Plate-and-frame filter presses of wood or bronze are used for clarifying the solution. Although free of copper and acid, zinc-sulphate solution will cause iron plates to rust quickly, thereby plugging solution passages. All pumps and solution lines for handling acid solution are made of lead and those handling neutral solution containing any copper are made of bronze and copper. No satisfactory substitute for lead for pumping and conveying acid solution has been found.

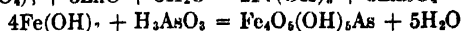
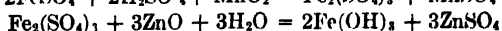
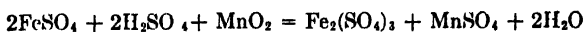
**Leaching.**—The primary object of leaching is to dissolve all zinc oxide and zinc sulphate contained in the roasted concentrate in dilute sulphuric acid according to the reaction of  $\text{ZnO} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2\text{O}$ . Unfortunately, some iron, arsenic, antimony, silica, alumina, copper, cadmium, and other metals are also dissolved and must be removed from solution prior to electrolysis. It is necessary completely to neutralize all sulphuric acid to insure removal of most of these impurities. This may be done as a continuation of the leaching operation by the addition of finely ground limestone or milk of lime, constituting what is known as "single" leaching. It is not possible to neutralize exactly all free sulphuric acid and precipitate the necessary impurities by addition of calcine. Some excess calcine is required to complete the reactions, resulting in a serious loss of zinc in the residue as undissolved zinc oxide. In order to allow the use of calcine for neutralization and precipitation of impurities, a leaching system is

employed whereby the residue from the first or neutralizing leach is treated with an excess of dilute sulphuric acid to dissolve all acid-soluble zinc, constituting what is known as "double" leaching.

"Single" leaching may be conducted as either a continuous or intermittent operation, but is more easily controlled if the intermittent or "batch" system is used. Calcine is added gradually to straight spent electrolyte until the acid strength is reduced to the lowest point possible and still obtain satisfactory recovery of zinc—0.3 to 0.5 per cent  $H_2SO_4$ . Finely ground limestone or milk of lime is added in sufficient quantity to neutralize the remaining acid with precipitation of iron, silica, alumina, arsenic, and antimony, and to coagulate the pulp to obtain good settlement of the residue and give a clear thickener overflow. With this system of leaching, the amount of zinc recovered depends upon the care of the operator in adding insufficient calcine to neutralize completely all acid and in giving a long enough period of agitation after the last calcine addition to insure extraction of all soluble zinc. Milk of lime, and, to a less degree, limestone will precipitate zinc from a neutral zinc sulphate solution, causing some loss of zinc. All acid neutralized by limestone or milk of lime must be replaced either by the addition of fresh acid or by increasing the amount of zinc sulphate formed in roasting. The  $CaSO_4$  formed increases the bulk and moisture content of residue. Finely ground limestone and milk of lime are quite an additional expense in the supply account. Normally, the only justification for the use of single leaching with dilute sulphuric acid is the saving in the cost of plant and in operating cost. A single set of leaching tanks and thickeners with necessary auxiliary equipment, such as classifiers, pumps, etc., is required for the application of this method of leaching.

"Double" leaching may be conducted as either a continuous or an intermittent operation, but is more economically applied as a continuous-leaching system when a large volume of pulp is to be handled. A plant producing a small daily tonnage of zinc, requiring a small volume of solution, should use intermittent or "batch" leaching for the first or neutral leach, thereby saving in first cost for building and leaching equipment more than enough to offset any additional operating cost. With the double leaching system, all of the calcine is added to part of the acid (spent electrolyte), giving an excess of zinc oxide for complete neutralization of acid present, precipitation of impurities, and coagulation of pulp. The discharge from this leach goes to thickeners, the spigot product from the thickeners being leached, with or without filtration, prior to leaching, with sufficient spent electrolyte to dissolve all zinc oxide and make the pulp distinctly acid—from 0.3 to 0.5 per cent  $H_2SO_4$ . This pulp goes to a second set of thickeners; the thickener spigot is filtered to give a final residue, and the thickener overflow and filtrate are returned to the first leach and are mixed with the remaining spent electrolyte to form the first leaching solution.

If the calcine does not contain sufficient soluble iron completely to precipitate all soluble arsenic and antimony, ferrous or ferric sulphate solution, prepared by leaching iron-bearing material with hot spent electrolyte, is added to the leaching solution for the first leach and is oxidized with manganese dioxide to ferric sulphate before adding calcine. Enough  $MnO_2$  is added to oxidize all ferrous iron dissolved from the calcine in addition to that derived from outside sources, such as scrap iron, siderite, or other readily soluble iron ore. The chemical reactions involved are:



The above reactions show that all sulphuric acid combined with iron is eventually used to dissolve zinc oxide and the iron is precipitated as ferric hydroxide, insoluble

in neutral or slightly basic solution. Some ferric hydroxide combines with soluble arsenic and antimony to form insoluble basic salts, thereby completely removing these elements from solution, provided sufficient ferric iron is present in solution.

The first leach is so controlled that a large excess of zinc oxide over that necessary to neutralize all acid present remains in the pulp. This hastens the precipitation of silica, alumina, iron, etc., and causes soluble silica to precipitate in a somewhat granular form, so that the pulp settles readily. Heat also aids these reactions and the higher the temperature the more complete the purification of solution and the better the coagulation of the pulp. As this is usually the only purification step for arsenic and antimony, the leach must be so controlled that it is known positively at all times that this purification is complete. A simple method has been adopted for detecting the merest traces of arsenic or antimony in solution. A hydrogen generator is set up, using pure zinc and sulphuric acid, and the gas is passed through lead acetate solution, to remove any traces of hydrogen sulphide, and then through silver nitrate solution. The solution to be tested is added to the hydrogen generator and the silver nitrate solution is watched for change in color. A trace of arsenic will give a brown discoloration and larger amounts will give a black precipitate. Arsenic shows up quickly, but small amounts of antimony will not show any discoloration for several minutes. Samples of the leach discharge taken at half-hour intervals are filtered and the filtrate tested for iron, arsenic, and antimony. The test for iron is the addition of a small amount of nitric acid to the sample of filtrate to oxidize any ferrous iron present, and adding potassium sulphocyanate to this solution. The depth of the red color indicates the amount of iron present and may be compared with standards to determine the exact amount.

Recovery of zinc in the first or neutral leach is low, usually not over 60 per cent of the acid-soluble zinc in the calcine being extracted, on account of the large excess of zinc oxide required for the complete precipitation of impurities. This necessitates adding practically half of the spent electrolyte to the second, or acid, leach. If the neutral-thickener spigot product is not filtered ahead of the acid leach, a large quantity of neutral solution is circulated, thereby increasing the volume of acid-thickener overflow and diluting the acid strength in the first leach to about one-third that of the spent electrolyte. This fact is not without some beneficial features, as the lower acid strength of leaching solution dissolves correspondingly less impurities, notably silica, copper, and iron, and simplifies purification and settling. Some copper dissolved from the calcine is precipitated from solution by the excess zinc oxide, but is redissolved in the acid leach and is returned to the neutral leach in acid thickener overflow, unless this solution is passed over scrap iron before being returned. At Trail, all spent electrolyte is added to the second leach, only acid-thickener overflow being used in the "neutral" leach. With this system the "neutral" leach is only a purification operation, very little zinc being dissolved.

The object of the second or "acid" leach is to recover as much of the acid-soluble zinc as possible and the least quantity of impurities, as any impurities dissolved must be returned to the first leach. Spent electrolyte is added to the thickened or filtered neutral pulp, in quantity sufficient to insure excess acid in the leach discharge. The amount of excess acid added largely determines the amount of impurities dissolved. If sufficient time is given for the leaching operation, practically all acid-soluble zinc will be recovered with less than 0.5 per cent acid in the leach discharge, and only a small part of the total impurities. Figure 8 gives graphically the behavior of some of the soluble impurities in the first and second leaches. Some of the impurities dissolved in the second leach are derived from the excess calcine added in the first leach, and, if the acid strength is carried as high in the second leach as in the first leach, more impurity will be dissolved, because there is much less zinc oxide present to neutralize the acid, giving it a greater opportunity to act on the impurities. Until all iron,

arsenic, antimony, etc. that are soluble in an acid solution of given strength are dissolved from the pulp, the acid-thickener overflow is a saturated solution of these impurities for that acid strength. Leaving the volume of solution constant, more or less of these impurities will be dissolved if the acid strength is increased or decreased. Therefore, if either the volume or acid strength of acid-thickener overflow is increased, the amount of impurities circulated will increase up to the point where all of these elements soluble in the existing acid strength has been dissolved, or if either or both the volume and acid strength of thickener overflow is decreased, less impurities will be circulated. It is highly desirable to keep the volume of solution and the amount of impurities circulated at a minimum, thereby facilitating settling in both neutral and acid thickeners and decreasing the volume of solution to be handled, giving more time for leaching in the same equipment. This can best be accomplished by filtra-

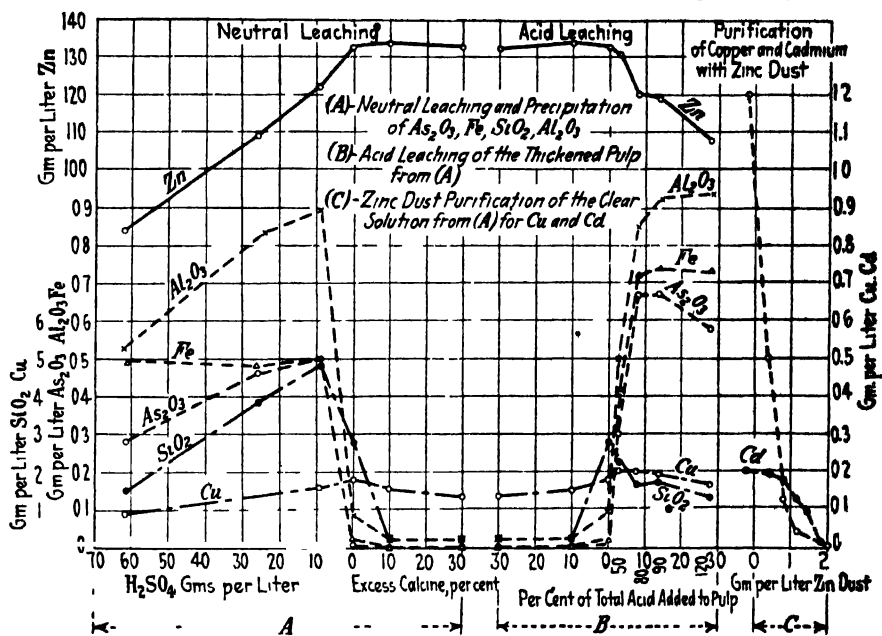


FIG. 8—Behavior of soluble impurities

tion of the neutral-thickener spigot product ahead of the second leach, returning the filtrate to the neutral-thickener overflow instead of circulating this amount of solution through the leaching and settling system, and returning it to the neutral leach for purification and settling the second time. Dissolving more zinc in the first leach will reduce the amount of solution required in the second leach, but carrying this too far is dangerous practice, as some excess zinc oxide is necessary for complete precipitation of impurities and for coagulation.

Acid-leach pulp does not settle so rapidly as properly coagulated neutral pulp. Therefore, some fine solid material overflows the acid thickeners and is put back into the neutral system, constituting an additional burden on this equipment. The amount circulated depends partly upon rate of flow through the thickeners. Therefore reduction in volume of solution passing through the acid system will reduce the amount of solids as well as the amount of impurities returned to the neutral system.

An apparently simpler method of accomplishing the desired results from the double-leaching system would be to treat all spent electrolyte with calcine in sufficient

quantity to reduce the acid content of the leaching solution to about the same strength as the acid-thickener overflow—0.3 to 0.5 per cent  $\text{H}_2\text{SO}_4$ —and neutralize and purify the resulting solution with some excess calcine or limestone as a separate step; if calcine is used, returning the residue to the leaching system, or if limestone is used, discarding the residue. Under this system, more impurities are dissolved from the calcine, due to high acid strength in the leach, and the purification residue settles very slowly and is difficultly filterable. Precipitated hydroxides and gelatinous silica require the weight of the main body of the residue to carry them down in the thickeners, and also filter much more readily when mixed with the sandy portion of the residue. Several attempts have been made to use a separate purification step, but none has proved so successful in operation as the double-leaching system just described.

**Purification of Neutral Solution.**—Neutral-thickener overflow is free of iron, arsenic, antimony, silica, and alumina, if the neutral leach is properly carried out, but contains from 40 to 60 per cent of the copper contained in the calcine and most of the cadmium, as well as some silver, nickel, cobalt, etc., if present in the ore. Copper and cadmium are the impurities more commonly found in appreciable amounts in this solution. Copper must be removed to avoid troubles in the electrolytic cells, and cadmium must be removed to produce grade A zinc. If these are the only metals to be removed, agitation of the solution with finely divided particles of metallic zinc will accomplish the desired result. Atomized zinc is commonly used for this purpose and high efficiency may be obtained from the zinc dust used for the removal of copper down to trace amounts. The elimination of the last of the copper content requires some excess zinc, and the removal of cadmium requires an excessive amount of zinc, even with mechanical agitation. Most of this zinc may be recovered, however, by retreatment of the purification residue or sludge and does not constitute a total loss.

If all arsenic is not removed in the neutral leach, some will be precipitated with copper by zinc dust. It is possible completely to precipitate arsenic from solution by means of zinc dust, if the solution is heated and sufficient copper sulphate is present. At Hobart, Tasmania, this method of purification has been elaborated slightly to provide a method for the removal of cobalt from solution. The problem of cobalt purification was a serious menace to the successful treatment of their concentrate, until they adopted the method of adding arsenic and copper to the neutral solution before zinc-dust purification, and precipitating the three metals together by means of agitation with zinc dust.

Cadmium is really precipitated more rapidly than copper, when zinc dust is first added to the solution, but almost immediately replaces copper in solution and remains to be precipitated by subsequent addition of zinc dust. Therefore, practically, copper is largely removed before much cadmium is precipitated. If grade A zinc is not desired and cadmium in the zinc slabs is not objectionable, copper may be precipitated sufficiently completely for successful electrolysis and yet leave some cadmium in solution, thereby reducing the amount of zinc dust required. Finely divided particles of cadmium oxidize rapidly if air agitation is used, and are redissolved in neutral zinc sulphate solution. This is the reason for cadmium "coming back" in neutral solution after once being precipitated— $\text{CdO} + \text{ZnSO}_4 + \text{H}_2\text{O} = \text{CdSO}_4 + \text{Zn(OH)}_2$ —and is the basis for one scheme for separation of zinc and cadmium.

Any silica not removed from solution in the neutral leach is precipitated by zinc dust in the purification tanks, increasing zinc-dust requirements, and later "blinding" the filter cloth in the clarification filters. Solids overflowing the neutral

thickeners will also increase zinc-dust consumption and increase the burden on the clarification filters. To obtain the highest efficiency from zinc dust, the solution to be purified should be free from mechanically held impurities and from such soluble impurities as silica, ferric sulphate, and free acid. Ferric sulphate and free acid will redissolve cadmium and increase zinc-dust consumption.

Control of purification is so variable that continuous purification is not safe practice and the operation is carried on under a "batch" system, using mechanical agitation. A tank is filled and agitated with zinc dust until copper is removed, as shown by  $H_2S$  test. An additional quantity of zinc dust is then added and agitation continued for a given period of time to insure removal of cadmium, or all the zinc dust required may be added at once and agitated for a given period. The amounts of zinc dust and the time required for agitation must be determined experimentally for the particular class of ores being treated, as there is no satisfactory rapid method known for detecting small amounts of cadmium in the presence of large amounts of zinc.

The discharge from the purification tanks is either filtered direct in a pressure filter to remove copper-cadmium sludge, or is first sent to settling tanks to relieve the load of solids from the pressure filters. Filtration of the solution at this point must be perfect and the filtered solution should be crystal clear. Any solids going through the filter will certainly cause trouble later in the electrolytic cells. If the solid particles are copper or cadmium sludge, they will be dissolved by the acid in the cells and impair either ampere efficiency or quality of metal produced, or both; if the solids are particles of residue overflowing the neutral thickeners, arsenic and antimony will be dissolved in the cells. Settling alone is not sufficient to insure the necessary clarity of solution. The filtered solution is sent to storage tanks supplying the electrolytic cells and, if the neutral leach and purification steps have been properly carried out, is free of physical or chemical impurities injurious in the electrolytic cell.

Some ores contain antimony in sufficient quantities to complicate the usual neutral-leach purification and require some additional purification step following the neutral leach. Neutral solution may be acidified to 0.5 to 1 per cent acid and treated with hydrogen-sulphide gas to remove arsenic, antimony, copper, and cadmium. It is difficult to remove the last trace of antimony in a reasonable length of time by this method, requiring storage space to allow time for completion of the reaction. Settling and filtration of the precipitated antimony sulphide is difficult, due to the extremely finely divided state in which it comes out of solution. The presence of copper in solution aids the precipitation and filtration.  $H_2S$  is both obnoxious and poisonous, requiring special care and equipment for application on a large scale. The only large-scale application of this method of purification was in the treatment of fume from the Mammoth smelter at Kennett, Cal.

Fume from the reverberatory smelting of complex ores was treated in the plant at Keokuk, Iowa, using a special purification step for the removal of arsenic and antimony. Ferric iron, either hydroxide or sulphate, was added to the zinc sulphate solution, slightly acidified, and neutralization was completed by addition of milk of lime. The resulting ferric hydroxide precipitate carried all the arsenic and antimony contained in the solution, and was removed as a separate residue. Owing to the gelatinous nature of such a residue, or precipitate, filtration and washing is a difficult problem, and a serious loss of zinc as entrained solution is almost certain.

**Filtration.**—What is probably the most serious problem in the filtration of the slightly acid pulp from the thickeners following the acid, or second, leach is washing the filter cake to avoid loss of zinc as entrained solution in the final residue. The gelatinous precipitates of iron and aluminum hydroxides and silica in the pulp form a cake more or less impervious to the passage of wash water.

If low-grade zinc concentrate is being treated, there is a high proportion of sandy material to gelatinous material in the residue and the cake may be washed with sprays. As the zinc content of the concentrate increases, the proportion of gelatinous to sandy material increases and washing becomes more difficult, finally reaching a point where sprays cannot be used satisfactorily and washing by dilution must be used. A normal residue filter cake from concentrate containing 30 to 35 per cent zinc will contain about 25 per cent moisture, while the residue from concentrate containing 55 per cent zinc will carry 35 per cent moisture or more.

Washing by replacement is more efficient and requires less water than washing by dilution, and is also much less expensive. In either case, hot water is more efficient than cold. The viscosity of zinc sulphate solution increases with decrease in temperature and, as the viscosity increases, it is less readily miscible with water. Heating the pulp to be filtered will not only increase the capacity of a filter, due to freer passage of solution, but will also decrease the moisture content of the filter cake. The amount and the method of washing is partly governed by the zinc content of the solution in the pulp being filtered. As the zinc content of the solution increases, the loss of water-soluble zinc increases, unless additional washing is provided. A combination of washing by replacement and by dilution is generally used. Spray washing is used first and the resulting cake is repulped with hot water, in a suitable agitator, the resulting pulp being refiltered on a second filter, using spray washing. If the amount of zinc to be recovered will pay for the cost of the operation, a second repulping and refiltration is employed. If the residue is to be treated in a lead blast furnace, any penalties imposed on zinc by the smelter, freight, and treatment charges are credits against the cost of washing, in addition to the value of zinc recovered. Repulping may be done in any satisfactory type of agitator, but an adaptation of a pug mill is one of the simplest and cheapest devices. A trough is fastened to the cake-discharge side of the filter to receive the cake as discharged. In this trough is a revolving shaft carrying pug-mill blades and driven from the filter-driving mechanism. Stuffing boxes are placed in each end of the trough to carry the shaft. Water is added to the trough in sufficient quantity to form a pulp of the proper density, the discharge from the trough being fed to a second filter. The amount of wash water that can be used is limited by the moisture carried out in the residue and the amount evaporated throughout the plant, unless some solution is discarded for other reasons.

Pulp fed to the filters should be sufficiently thick to prevent much classification in the filter tank, and some means of agitation should be provided so that a constant proportion of sandy material is maintained in the cake. If the pulp is too thin, sand will settle out in the filter tank, and the filter cover will become "blinded" with slime.

As high vacuum as possible should be maintained in order to reduce the moisture in the cake to a minimum and to keep the capacity of the filter at the maximum. The dry-vacuum system is much to be preferred, but must be provided with large solution receivers and moisture traps to avoid carrying solution or spray into the vacuum pumps. A slight leakage of solution or spray will soon corrode the valves and the cylinders of the pumps to a point where they lose efficiency and will in a short time cause more serious trouble through breaking of valves and pistons. Traps and receivers made of wood staves are preferable to steel tanks with lead linings. Lead linings tend to collapse and break along the seams, giving the solution a chance to corrode the tank shell, and are expensive to maintain.

**Treatment of Copper-cadmium Residue.**—Residue produced by purification of solution with zinc dust contains too much excess zinc to be discarded and usu-

ally carries sufficient cadmium to pay for treatment to recover this metal. Some basic zinc sulphate precipitates during purification and clarification and some recoverable zinc overflows the neutral thickeners, all of which is recovered, together with the excess zinc dust, as purification sludge or residue in settling tanks and in the clarification filters. The amount of zinc in this material is usually just about equal to the amount of zinc dust used, and, if not retreated, would result in a considerable loss of zinc. Treatment of this material is, therefore, necessary from the zinc-recovery standpoint, and, in addition, its copper content is concentrated into a much smaller quantity of residue, and most of the cadmium is recovered for market.

If purification residue is roasted to increase the solubility of zinc and cadmium, by conversion from metallics to oxides, the copper content is also converted to oxide and, when treated with dilute sulphuric acid, nearly as high a percentage of copper as of zinc and cadmium is dissolved. Oxidation of these metals is fairly rapid if purification residue is allowed to remain in contact with the air for any great length of time. If purification residue is treated with dilute sulphuric acid (spent electrolyte), before much oxidation has taken place, only a small part of the copper is dissolved, but most of the zinc and cadmium go into solution. Addition of sufficient residue completely to neutralize all acid will supply enough excess zinc to precipitate practically all copper from solution, giving a residue containing all of the copper in the original purification residue and less than one-third of the zinc and cadmium, and a solution low in copper and containing over two-thirds of the zinc and cadmium. The residue so produced is a desirable material for a copper smelter. The neutral zinc-cadmium solution is heated to 75 to 80°C. and circulated slowly through tanks in which are suspended zinc slabs, thereby precipitating cadmium as a spongy deposit on the zinc slabs. This sponge oxidizes rapidly in drying, giving a dried product containing about 60 per cent cadmium and from 5 to 10 per cent zinc, and may be marketed as such. If metallic cadmium is desired, cadmium sponge is dissolved in dilute sulphuric acid and the resulting solution is electrolyzed at a current density of 10 to 15 amp per sq. ft. of cathode surface, using lead anodes and aluminum cathodes. The solution, after passing over zinc slabs, contains all the zinc recovered and little cadmium, and is returned to the main zinc-solution system, being added to the neutral leach for purification of any iron and arsenic which it may contain.

If grade A zinc is not desired and cadmium is not to be recovered separately for market, the solution from leaching purification residue may be returned to the neutral leach direct without precipitating cadmium as sponge.

Purification residue may contain some arsenic, due to imperfect purification in the neutral leach, and always contains metallic zinc. When treated with dilute sulphuric acid, hydrogen is generated, and arsine, if arsenic is present. A very little arsine will cause serious illness and very probably will result in death. It is, therefore, absolutely necessary to provide every possible safeguard in a plant of this kind. The purification residue treatment plant should be in a separate building, well ventilated, and the leaching tanks should be hooded and connected to an exhaust fan of ample capacity to maintain a constant vacuum in the tanks and hoods. Samples of air should be drawn continuously from different parts of the plant and passed through lead acetate solution to remove  $H_2S$  and then through silver nitrate solution, which will indicate the presence of any arsine. Such samples should be drawn from near the surface of settling tanks and from the floor of the building. As the arsine is heavier than air, it will concentrate in low places and might remain unnoticed until some disturbance in the atmosphere of the building would distribute it and result in poisoning every employee in the department.



Ores containing little or no copper, but some cadmium, will produce purification residue, which may be treated by a different method for the recovery of zinc and cadmium. The residue is roasted at a low temperature completely to oxidize all cadmium and the resulting calcine is leached with neutral zinc sulphate solution, thereby dissolving cadmium and precipitating zinc from solution according to the reaction,  $\text{CdO} + \text{ZnSO}_4 + \text{H}_2\text{O} = \text{CdSO}_4 + \text{Zn(OH)}_2$ . It is possible so to control the addition of calcine that a solution of  $\text{CdSO}_4$ , which may be electrolyzed direct, is produced. The resulting residue is treated for the recovery of zinc by leaching with dilute acid.

The market for cadmium is so limited that, if all the cadmium which it is now possible to produce by electrolytic-zinc plants was recovered and placed on the market, some time would elapse before new uses could be sufficiently developed to absorb the production. Very little cadmium produced from this source has been marketed as metallic cadmium, although the product is of exceptionally high purity, containing over 99.97 per cent cadmium. As new uses for the metal develop, more attention will be paid to this source of supply, the amount of which is now greater than the entire present consumption of cadmium in the United States.

**"Continuous" vs. "Batch" Leaching.**—The continuous leaching system employed in the large plants now operating is well adapted to plants handling a large volume of solution and having a fairly uniform feed. Sudden changes in the analysis of feed make close control of the purification part of the neutral leach almost impossible, and are sure to result in improperly purified solution getting by to the electrolytic cells unless the leach is operated continuously under conditions suited to the maximum amount of impurities. With a batch-leaching system, each tank of solution can be held until its purity is assured. A larger proportion of the zinc content of the calcine is recovered in the neutral leach with the batch system, as more time can be given for adding calcine and for agitation between additions and a closer control can be had of the amount of calcine added in excess of that necessary for neutralization. This results in less acid-thickener overflow returning to the neutral leach and improves conditions generally in the acid leach.

Air consumption is greater with the continuous system than with the batch system, for a small plant, as it is necessary to maintain agitation in all of the tanks for the full 24 hrs. to prevent settling and plugging of air lifts, while under the batch system each tank is completely emptied at the end of each leach and air is used only during the actual period of leaching. A plant producing 50 tons of zinc per day will require less than 1,000 tons of solution per 24 hr. This amount of solution can be handled more economically and with better leaching results in the same number of tanks operating independently than if arranged in series. As the volume of solution increases beyond the capacity, if operated independently, of the minimum number of tanks that can be placed in series for successful continuous leaching, the comparison changes in favor of continuous leaching, due to the saving in time required for filling and discharging.

Labor and repair charges are lower with continuous leaching and the entire leaching operation is simplified. The capacity per tank is greater, giving fewer units for leaching and for calcine storage. Also, less difference in elevation is required between leaching tanks and thickeners, as the tanks are discharged from the top instead of from the bottom.

In general, plants of small capacity and those having a very variable feed are best served by the batch system, and those of large capacity and having an uniform feed are best served by the continuous system for the neutral leach. For the acid leach, the continuous system is preferable for all plants.

**Recovery of Zinc from Residue.**—Residue from the treatment of any concentrate containing iron will contain some undissolved zinc in the form of ferrate. It will also contain some undissolved zinc oxide in the very small lumps which have not been penetrated by the leaching solution, any zinc sulphide remaining in the calcine, and some zinc sulphate as entrained solution. The higher the zinc content of the concentrate the smaller the percentage of the total zinc that remains in the residue. Less total ferrate is formed in roasting, due to the lower iron content of the concentrate; less sulphide sulphur remains in the calcine, due to the higher permissible roasting temperature. The amount of zinc so combined is a smaller percentage of the total, and less residue is produced, thereby decreasing the possibility of losing solution and allowing more wash water to be used per ton of residue.

Regardless of the percentage of total zinc in concentrate that is contained in the residue, the residue may contain enough zinc, per ton of residue, to warrant special methods of treatment for its recovery and show a profit. On the other hand, the loss of zinc per ton of concentrate in residue may be excessive, yet the zinc contained per ton of residue may be too low to pay for cost of treatment. Assuming that 95 per cent recovery of zinc can be obtained from a concentrate containing 60 per cent zinc and that 0.2 ton of residue is produced per ton of concentrate, the residue will contain 15 per cent zinc. Also, assuming that a recovery of 80 per cent of zinc can be obtained from a concentrate containing 30 per cent zinc and that 0.65 ton of residue is produced per ton of concentrate, the residue will contain 9.25 per cent zinc. The first residue is an attractive one to treat, while the other is so low in zinc that conditions would need to be especially favorable to pay the cost of treatment.

Evaporation of spent electrolyte to 50°Bé. acid and mixing with dry residue so that 1.75 lb.  $\text{H}_2\text{SO}_4$  is added for each pound of zinc in residue, and gradually heating the mixture to between 600 and 650°C. will decompose both zinc ferrate and zinc sulphide, forming zinc sulphate, and will decompose iron sulphate, leaving a material from which zinc and copper can be extracted by water leaching without dissolving much iron. If the temperature is not carried over 600°C., all iron sulphate will not be decomposed in a reasonable length of time, with the result that some iron will be dissolved and a low extraction of zinc will be obtained with a water leach. The reaction between  $\text{ZnO}$  and  $\text{H}_2\text{SO}_4$  does not appear to be direct in the decomposition of ferrate by this method, iron sulphates being formed first. As their decomposition progresses with increased temperature, zinc sulphate is formed.

A high recovery of zinc can be obtained by this method—from 75 to 80 per cent of the zinc in residue—but there are two serious difficulties to be overcome. Evaporation of spent electrolyte to 50°Bé. acid is not a simple problem, due to crystallization of zinc sulphate as the concentration increases, 50°Bé. acid retaining only a trace of zinc. Depletion of the solution electrolytically before evaporation can be carried down to about 0.5 per cent zinc, but only at expense of ampere efficiency. If roaster gases are utilized for acid manufacture, it would be cheaper to deplete spent electrolyte of its zinc content and discard enough of this solution to offset the addition of fresh acid. A second difficulty to be overcome is the handling and roasting of the mixture of residue and acid. When first mixed, a residue containing 10 per cent zinc and the necessary amount of acid form a mixture too thin to be handled in the usual types of large-scale drying equipment. As drying progresses and the temperature is raised, the mixture builds up rapidly on the dryer hearth or lining, forming a coating of extreme hardness.

In addition to the recovery of zinc and copper, this method of treating residue has an advantage over other leaching methods, in that the water-leached residue settles

and filters readily and can be washed reasonably free of entrained solution. Iron, arsenic, antimony, and other objectionable impurities, except copper and cadmium, are not dissolved by the water leach, making the purification of the resulting solution a simple matter.

An equally high extraction of zinc can be obtained by leaching residue with a large excess of 25 per cent  $\text{H}_2\text{SO}_4$  solution at 90 to 100°C., keeping the final acid strength above 15 per cent  $\text{H}_2\text{SO}_4$ . The disadvantages of this method of treatment are that nearly all iron, arsenic, antimony, etc., are redissolved, and, when reprecipitated by neutralization of the remaining acid, a very difficultly filterable residue is produced. The excess acid may be neutralized with roasted cathode-melting-furnace dross, or with high-zinc calcine, to a point where sufficient iron has been precipitated to remove most of the arsenic and antimony. Acid of the necessary strength is supplied by evaporation of depleted spent electrolyte, concentration being carried this far without much crystallization of zinc sulphate. Unless a pressure filter is used, the leached pulp is diluted with water to avoid crystallization and is thickened in the usual manner before filtration, the slightly acid solution being sent to the neutral leach for final purification.

At Trail, residue has been treated at 500 to 550°C. in a current of  $\text{SO}_2$  gas, forming zinc sulphate from zinc ferrate. Some iron sulphate is also formed and, unless the temperature is later raised to 600°C. or higher, iron will be extracted with the zinc by water leaching. Very satisfactory recovery of zinc was obtained by this method of treatment, the final residue being nearly free of zinc. As in sulphate roasting, the problem of the disposal of the acid formed in roasting must be solved to make this method successful. In order to recover any zinc present as zinc sulphide, residue from acid leach, at Trail, is sent to flotation machines. The concentrate produced is returned to the roasters.

**Electrolysis of Zinc Sulphate Solution.**—When the leaching and purification operations have been properly carried out, the zinc sulphate solution delivered to the electrolytic cells is practically entirely free from impurities that may be injurious to the operation of the cells. It is of the greatest importance to the success of the entire process that the solution be as nearly free from metals electronegative to zinc as it is possible to make it, because the electrolytic zinc cell is extremely sensitive to the effect of some impurities, under any conditions, and is noticeably sensitive to others present in minute quantities, under usual operating conditions. The effect of some impurities may be minimized by changing conditions or by use of certain addition agents, such as glue, but purity of solution is the only absolute guarantee of satisfactory results.

Next in importance to purity of solution is the purity of electrodes and tank-lining material. The purest lead obtainable should be used for anodes and tank lining, if wooden tanks are used, and aluminum of the highest purity should be used for cathodes.

With these essential details taken care of, the electrolytic zinc cell will allow of a reasonably wide variation in operating conditions, such as temperature, acidity, current density, etc., without much change in ampere efficiency. As these conditions will affect the voltage required, and thereby the power requirement, they are all of importance in the economic success of the process.

**Power Equipment.**—Rotary converters, having suitable voltage control, are the most efficient machines for conversion of alternating to direct current and are best suited to the needs of the process. Power is normally the largest single item in operating cost, and the power requirement of the zinc cell is so great that the

smallest possible conversion loss amounts to a large sum. Rotary converters installed at Great Falls have a conversion efficiency of about 93 per cent, as compared with 85 to 88 per cent for motor-generator sets. The higher voltage of the rotary converter permits more cells to be connected in series, requiring fewer

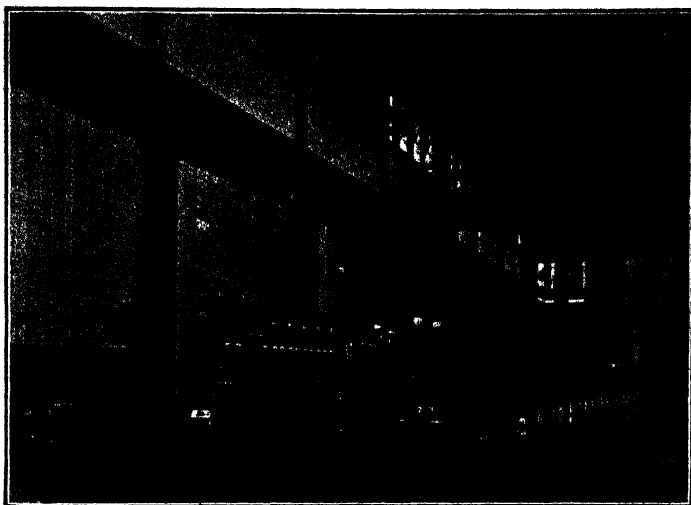


FIG. 9.—Rotary converters at Great Falls zinc plant substation.



FIG. 10.—Great Falls tank room (showing stripping racks, lifting frames, cathode cars, and method of insulating chain blocks from trolleys).

units. Grounding of the neutral point of each circuit lessens the possibility of personal injury with the higher voltage; at Great Falls not a single injury has resulted in the 10 years' operation using voltages of from 500 to 550 volts per

unit. Larger and fewer units require less attendance and less floor space, making both first cost and operating cost less.

**Tanks.**—Wood or concrete, or possibly brick, may be used for cell construction. Where wood is used, cells are lined with chemical lead and are held together at the ends with iron bolts and plates, as they must resist the pressure of the load of solution, electrodes, and bus bars, unless the bus bars are carried independently of the tanks. If concrete is used, the cell is lined with sulphur-sand cement, which is acid proof and also a good non-conductor. Various kinds of asphalt linings have been used without success. The size of tank required will depend upon the number and the size of electrodes and the spacing between electrodes—4-in. spacing from center to center of anodes is generally used. Some space must be provided below the bottom of the electrodes for settlement of the manganese dioxide sludge deposited at the anode and sufficient clearance must be allowed between electrodes and the tank side to avoid striking the tank lining when removing electrodes. Lead overflow lips are burned to the tank lining. No provision is made for draining the tanks, as it has been found cheaper and more satisfactory to empty the tanks from the top with a pump than to provide drains and settling equipment underneath. Trail uses concrete tanks with sulphur-sand lining, two tanks being poured with a common center wall. A form is placed inside the tank and the hot sulphur-sand mixture is poured around the form.

**Electrodes.**—Aluminum sheets  $1\frac{1}{4}$  or  $3\frac{1}{16}$  in. thick, and of the highest purity, are used for cathodes. Copper support bars are riveted to these sheets, using copper rivets, and also act as conductor bars. Aluminum bars and rivets, and aluminum bars with copper rivets, have been substituted for copper bars, but the contact between aluminum and aluminum is not particularly good and excessive heating resulted. Sheets thicker than  $3\frac{1}{16}$  in. have been tried, but the surface of the aluminum has been bad, resulting in the sticking of the zinc deposit; also, the added weight is an objectionable feature in removing plates for stripping of the zinc deposit. Wooden strips are placed on the edges of the sheets to prevent zinc building around the edges. No strips are needed on the bottoms of the plates.

The anodes are cast chemical lead  $3\frac{1}{8}$  in. thick, the anode being cast around a copper support bar, leaving one end exposed to make contact with the bus bar. The anode is slightly smaller in cross-section than the cathode. Trail uses anodes having sufficiently heavy tops to support the body of the anode without using copper support bars and the anode is burned to the tank bar, which is a lead-covered copper bar.

The size of electrodes and number per cell will depend upon the capacity of plant, the current density, and other local conditions. If bus bars are carried on the edges of the tank, larger electrodes are required than if the bus bars are supported independently of the tank, due to greater distance between solution level and electrode support bars. The type of electrode support bar may be varied to suit local ideas or conditions, but must have sufficient current-carrying capacity to avoid heating, and must have sufficiently broad ends to avoid swinging or tipping of the electrodes. The electrodes must hang absolutely true to avoid short circuiting and insure an even distribution of current.

**Bus Bars and Tank Bars.**—Copper is universally used for bus bars, and may be either rolled or cast, cast bars being much cheaper than rolled or drawn bars.

If special shapes of large cross-section are required, cast bars are practically a necessity. The usual method of computing the size of bar required is to allow 1 sq. in. of cross-sectional area for each 1,000 amp., but with large bars, this does not allow enough radiating surface to avoid heating and should be increased to at least 1.25 sq. in. for each 1,000 amp. if 8,000 to 10,000 amp. is to be carried; thus, cast-copper bus bars having 10-sq. in. cross section are recommended for a circuit carrying 8,000 amp. For joining one length to another, the ends are machined for a lap joint and are bolted together. From time to time, it is necessary to tighten these bolts to insure perfect contact, especially if current is shut off, or materially reduced, from time to time, thereby causing alternate expansion and contraction, tending to pull the joint apart.

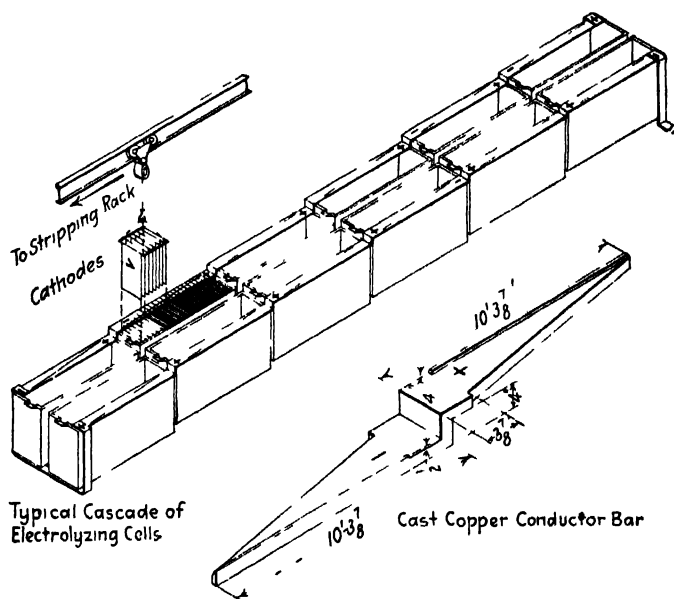


FIG. 11 Bus bar detail and arrangement

From the standpoint of first cost and of working conditions, triangular tank bars are the best. At the point of connection to the main bus-bar line, the anode tank bar has the same area as the bar line, but, as the current is distributed to the individual anodes, the area decreases to theoretical zero cross-section at the end of the tank. The cathode bar starts at zero cross-section and gradually increases in area as the load increases, until it reaches the full area of the bar line, and, passing to the next tank, becomes the anode bar and again gradually decreases in area to zero. With the exception of one anode and one cathode bar, all bars in each group of tanks in solution series are double bars. This system requires placing bars on only one side of the tank, putting insulated ends of both anode and cathode support bars on opposite side of the tank from the contact ends. Both anode and cathode contacts are on the working, or aisle, side of tanks, where they may be kept polished without leaning over the tank. The total amount of copper required on the tanks is only a little more than two-thirds of that required by a system using a common center bar, and about half that required if single bars are placed on each side of the tank. Figure 11 shows the design of a triangular bar used at Great Falls and the method of placing on tanks.

If the tank bars are carried on the edge of the tank, the contact ridge on the outside bar is made  $\frac{1}{4}$  in. higher than that on the inside bar, so that the electrode support bar extending to the outside tank bar will not come in contact with the inside tank bar. A much better system of supporting tank bars than that of placing on the edge of the tank was developed at Park City, Utah, whereby the bars are carried on independent supports placed by the side of the tank. With this system, the bars are placed on edge, instead of flat, and the contact edges extend above the edge of the tank just enough to allow the electrode support bars to clear the tank side. Triangular bars are also used in this system and no more copper is required than if placed on the edge of the tank. The advantages of the Park City system are that a greater percentage of the electrodes is rendered effective through reducing the space required between solution level and electrode support bars; contacts and tank-bar insulation are placed entirely outside of the tank, simplifying the problem of keeping contacts clean and keeping insulation dry; no acid mist or vapor comes in contact with the tank bars, avoiding corrosion, especially of the inside bar; a greater circulation of air around the bars is obtained, aiding cooling by radiation, and removing a heavy load from the side of the tank. The disadvantage of the system is the necessity of supplying greater aisle space.

**Insulation.**—Tanks are insulated from their foundations by placing glass blocks, or other insulating materials, between tank supports and foundations, and covering the insulators with caps of sheet lead to prevent wetting by solution leaks. Electrode support bars and tank bars are insulated from the tanks by wood strips and blocks impregnated with oil, tar, or other waterproofing material. Bus-bar lines are supported on glass blocks or are suspended by some type of strain insulators from tank or floor supports. Solution and water lines are insulated by breaking through rubber hose connections, and by supporting on wooden or tile blocks. It is essential that all insulation be made of non-absorbent material to avoid wetting by condensation of water vapor from evaporation in the cells and of mist carried by gas leaving the cells.

**Arrangement of Cells.** As many cells are placed in series, electrically, as the power equipment will permit—144 cells per unit at Great Falls with rotary converters, and 36 cells at Trail with motor-generator units. The maximum voltage limit of the direct-current equipment divided by 3.75 is a safe figure to use in determining the number of cells to be connected to one power unit. Normally, more cells could be carried, but some leeway is desirable. The present Trail and Great Falls plants were designed for a maximum of 4 volts per cell, but this figure is too conservative, as has been proved by later experience.

As many cells may be placed in series or cascade, as regards solution flow, as is desired, but, from the standpoint of working conditions and economy, six to eight cells in solution series are about the maximum number. A working aisle is provided on one side of each tank. The grouping at Great Falls is twelve cells to a group, or double cascade, two cascades of six cells each being placed side by side as closely as safe insulation will permit. Between each group of twelve tanks and the next group is a working aisle. Tank bars are placed on the sides of tanks next to the aisles, leaving the inside tank edges for insulated ends of electrode support bars. A working aisle and space for solution supply mains is provided between the upper tanks of cascades flowing in opposite directions, and stripping aisles and space for spent electrolyte launders are provided at the lower ends of the cascades. This arrangement is shown in Fig. 12.

By placing more cells in a cascade, less floor space and less copper would be required, but the cathodes would be transported further for stripping, requiring more operating labor. It is customary in cleaning tanks to cut out of the electrical circuit a double cascade at one time. Therefore the greater the number of tanks per cascade the greater the proportion of a unit cut out for cleaning. When any accident occurs, such as breaking of a solution feed line over a tank, or a roof leak, which will wash impurities into a cell and contaminate the following cells in the cascade, it is an advantage not to have many cells in series.

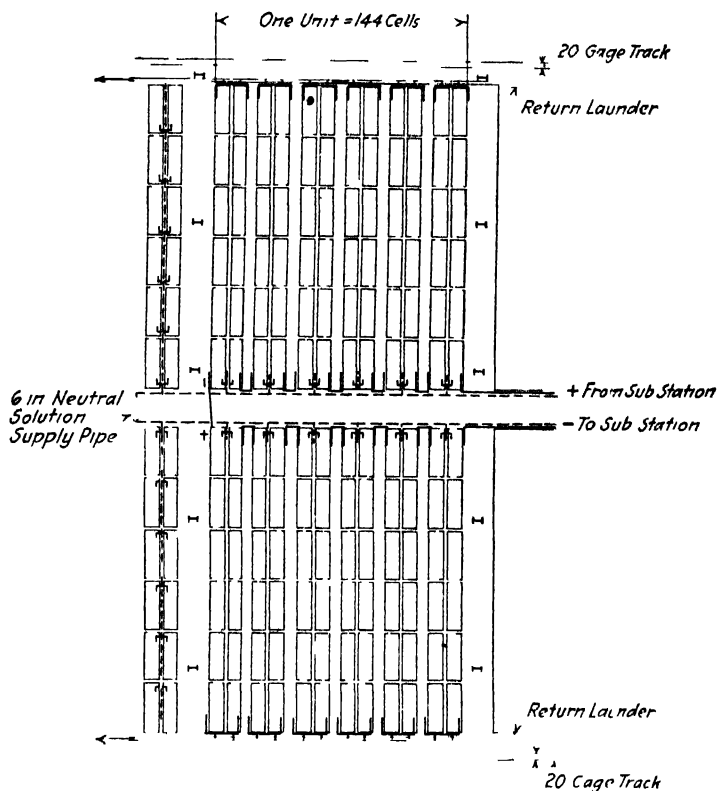


FIG. 12—Tank layout Circuit Cells

**Solution System.**—Purified solution from the leaching division is pumped into storage tanks placed at sufficient elevation to give gravity flow from storage to cells. Iron feed lines may be used, as this solution is neutral and practically free of copper. Lead lines with flanged joints are preferable, however, as some basic zinc sulphate is precipitated from solution as cooling progresses, and builds up in iron pipe more quickly than in lead pipe and there is always more or less danger of external corrosion of iron lines through occasional leaks of acid solution and condensation of acid mist coming from the cells. These lines are carried under the floor along the upper cells of the cascades and a 1½" 14 tapped in for each double cascade. A pipe line extending the full length of the cascade to the top of



the last cell is connected to this riser and may feed each cell of both cascades through branches equipped with valves to regulate the flow to each.

Solution is fed into the head cell of each cascade at a rate that will maintain the acid strength in that cell at slightly less than the discharge from the last cell of the cascade. The first cell discharges into the head of the second cell, the second into the third, and so on down the cascade, the last cell discharging into a launder emptying into storage tanks for the leaching plant. Neutral solution is fed into each cell but the last, in sufficient quantity to maintain practically constant acidity throughout the cells, above the last, in the cascade. The last cell brings the acidity up to the desired strength, or, looking at it the other way, depletes the zinc content to the desired point, thereby acting as the control cell. Samples of solution are taken at regular intervals from the last cell and the acid content determined, and at less frequent intervals from the upper cells to control the feed to each cell. By maintaining practically constant acidity in each cell, the voltage required is kept at a minimum. No acid solution is returned, to be mixed with the neutral feed solution to keep acidity in the upper cells up to the average, each cell generating its own acid requirements and receiving its own feed, except as the lower cells in a cascade receive the discharge from the cells above them.

The rate of flow increases from the first to the last cell, the volume being cumulative, but no improvement in efficiency of the cells having the higher rate of flow has been noticed. No baffle arrangement is necessary to maintain an even distribution of solution in the cell, the gas evolution at the anode being sufficient to supply the necessary circulation. As current density increases, rate of zinc deposition increases and also rate of evolution of oxygen at the anode, thereby increasing the rate of circulation proportionally to the requirement of fresh solution at the electrodes.

**Cooling.**—A large proportion of power delivered to the electrolytic zinc cell is dissipated as heat, the amount increasing with current density. Some heat is carried out by the spent electrolyte and some is radiated, but, at the current density usually employed in practice, it is necessary to supply some additional cooling. This is done by passing fresh water through lead coils placed in the ends of the cells. Each cell should be equipped with 50 ft. of cooling coil if a current density of 30 amp. per square foot or over is to be used. The amount of water required depends upon the temperature of the water and the efficiency of transfer of heat, in addition to cell conditions, such as current density, acidity, electrode spacing, etc., but in any case is quite large, varying from 6 to 8 gal. per minute for each ton of daily zinc production.

**Stripping Equipment.**—All methods—from removing one plate at a time for stripping and removing all plates in a cell at one time—have been tried. Removing one plate at a time is too slow and expensive, and removing a full tank at a time means loss of production and danger in “shorting” the tank before removing the plates, in addition to requiring some power-driven lifting device. If many plates are removed at one time, the current density on the remaining plates is greatly increased. Removing nine plates out of a total of twenty-seven leaves enough to carry the current and makes a very suitable weight to be handled with a hand-operated chain block when operating at 30 amp. per square foot and using a 48-hr. stripping interval.

A lifting rack having saw-tooth sides, the teeth being spaced 4 in. center to center to correspond with electrode spacing, is placed on the cathode support bars, and, as the load is lifted, the spaces between the teeth of the rack engage lugs riveted to the

cathode support bars holding the cathodes at the same spacing as in the cell. The chain block used for lifting the load is suspended from a trolley running on an I-beam over the center of the line of tanks. A strain insulator is placed between the chain block and the trolley to insulate the chain block and load from the I-beam. At the lower end of the cascade is placed a stand having nine pieces of 3 in. channel iron spaced 4 in. center to center, with a slot cut in the center of each piece. These pieces are supported at one end by bolting to the stand, the bolts being placed loosely enough to permit swinging in a horizontal plane. A load of plates removed from a cell is brought to this stand and the cathode sheets are slipped into the slots cut in the pieces of channel. The load is lowered until the cathode support bars rest on the channels and the lifting rack is disengaged from the lugs. The outside sheet of zinc is removed, then the channel supporting that cathode is swung to one side and the inside sheet of zinc is removed from that cathode. The adjacent side of the second cathode is then stripped and the second channel is swung over against the first, exposing one side of the third, and so on until all nine have been stripped. They are now swung back into the original position and lifted with the lifting rack, just as they were originally lifted from the cell, and are transferred back to the cell from which they came, being held correctly spaced in the lifting rack.

A heavy knife is used for stripping the deposit. The zinc deposit is struck a sharp blow with the edge of the knife to loosen it slightly from the surface of the aluminum cathode blank. The point of the knife is slipped under the zinc sheet and twisted to break the deposit loose. The zinc sheets, as stripped, are placed on a small narrow-gage car to be transferred to the melting furnaces.

**Operation of the Cells.**—Starting with clean cells, new electrodes, and neutral solution, the resistance is so great that little current flows for several hours after power is put on the circuit. It is customary, when starting a unit that has been down for some time, and from which the acid solution has been removed, partially to fill the cells with spent electrolyte from other units still operating, thereby reducing resistance so that some current will flow immediately. If no pure acid, such as spent electrolyte, is available, the flow of current is permitted to increase as rapidly as decreased resistance, through formation of acid in the cells, will permit. Some resistance may be removed by "shorting" one of two groups of cells until some current is flowing.

Zinc deposited in the first 24 or 48 hr., starting with neutral solution, will be rather spongy, due to low acidity, and should be stripped as soon as thick enough to break loose from the cathode. As soon as the deposited zinc begins to show a bright surface, the period of deposition is lengthened to 48 hr. When the acid strength gets up to 2 or 3 per cent, a small flow of fresh solution is started in the upper cells and is gradually extended to the lower cells as the acidity increases, so that no cell will become impoverished. Acid strength is not allowed to get above about two-thirds normal until the full period of deposition is started, and frequently full current density is not permitted until deposited zinc has been stripped once or twice.

One man can care for and strip zinc from 18 cells when using a 48-hr. stripping interval. Nine tanks are stripped each day and the load of zinc sheets is pushed over the scales and delivered to the melting furnace. With this system, 10,000 lb. of zinc per day is about the maximum that a man can handle over any considerable period. After a load of plates is lifted so that the bottoms are above the solution in the cell, it is allowed to drain into the cell, while the stripper polishes the tank-bar contacts from which plates have been removed. After zinc deposit is stripped, cathode contacts are polished and any cathodes having smooth spots on the depositing,

surface are roughened slightly, with a wire brush or piece of hack-saw blade, to prevent the zinc deposit springing loose. Cathodes must be replaced just right to insure an even distribution of current and a maximum power efficiency. If a cathode becomes slightly warped, it is nearly impossible to avoid "shorting" to one anode or the other. Therefore the stripper must also straighten any plates that are not exactly true. Wooden strips are placed on the edges of the cathode to prevent zinc from building around the edge. Rubber inserts, grooves, and other devices for accomplishing the same purpose have proved less satisfactory.

Many ores contain manganese, and some manganese dioxide is used to oxidize iron in the neutral leach. Part of the manganese in solution is precipitated at the anode as manganese dioxide, some of which adheres to the anode as a flaky covering, and the remainder settles to the bottom of the cell. Insulation on top of the cells gradually becomes impregnated with solution, and copper and zinc sulphates build up on the tank bars, if carried on the edge of the cells. Periodic renewal of insulation and cleaning of cells and bars is necessary. A double cascade of cells is cut out of the electrical circuit, the electrodes are removed, solution is pumped out, manganese sludge is removed and sent to the leaching plant, and insulation is renewed. Tank bars are cleaned and replaced, electrodes are straightened and replaced, cells are refilled with solution, and the jumper bar is removed, putting the cells back into the circuit.

**Care of Workmen.**—Rubber shoes are supplied to insulate the stripper. Garments made of pure, unwashed wool stand the corrosion of acid solution from the cells much better than cotton or mixed wool and cotton. Great care must be given the hands of men coming in contact with acid zinc sulphate solution, or cracks and sores around the finger nails will result. Several thicknesses of ordinary cotton gauze are placed over the nose and mouth to absorb any spray rising from the surface of the cells. The gas is largely oxygen, but the coating or film around the bubble is solution and is very corrosive to the nasal passages. No occupational disease has resulted from this work, nor has any extra trouble been experienced in recent years in getting men for this work.

**Voltage.**—The theoretical decomposition voltage of zinc sulphate solution is approximately 2.35 volts, but the best operating conditions require from 3.25 to 3.50 volts, depending upon current density, temperature, acidity, spacing of electrodes, and period of deposition. With constant acidity, temperature, etc., voltage increases rapidly with increased current density, as is shown by Fig. 13. Resistance of solution is decreased by increasing acidity, quite markedly up to 10 per cent  $\text{H}_2\text{SO}_4$ , and more slowly above 10 per cent  $\text{H}_2\text{SO}_4$ . With 30 amp per square foot and 5 per cent  $\text{H}_2\text{SO}_4$ , the voltage required is about 4.0 volts per cell at  $35^\circ\text{C}$ ; increasing the acidity to 12 per cent reduces the voltage to 3.4 at the same temperature. If the temperature and the acidity are both increased, the decrease is even greater, as is shown by Fig. 13. High temperature is not desirable in the cell, from the standpoint of effect of impurities on ampere efficiency, but is an aid to reduction in power cost, if ampere efficiency is maintained. It certainly pays to supply solution of sufficient purity to the cells to allow reasonably high temperature and acidity to be maintained. At Great Falls, temperature of over  $50^\circ\text{C}$  has been maintained with a current density of 30 amp per square foot of cathode surface, for several weeks at a time, and an ampere efficiency of 90 per cent obtained by cutting the period of deposition to 24 hr. The distance between the face of anode and the face of the cathode affects the voltage required, but cannot safely be reduced much below present practice on account of the

tendency of electrodes to warp, and because they do not hang absolutely true, due to unevenness in the surface of contacts between support and tank bars.

**Ampere Efficiency.**—Purity of solution, temperature of the cell, period of deposition, and ratio of zinc to acid in solution are factors influencing ampere efficiency. Some impurities may be present in much larger amounts than others without seriously affecting ampere efficiency, and much work has been done to determine the effect of single impurities and to set safe limits for the amounts that

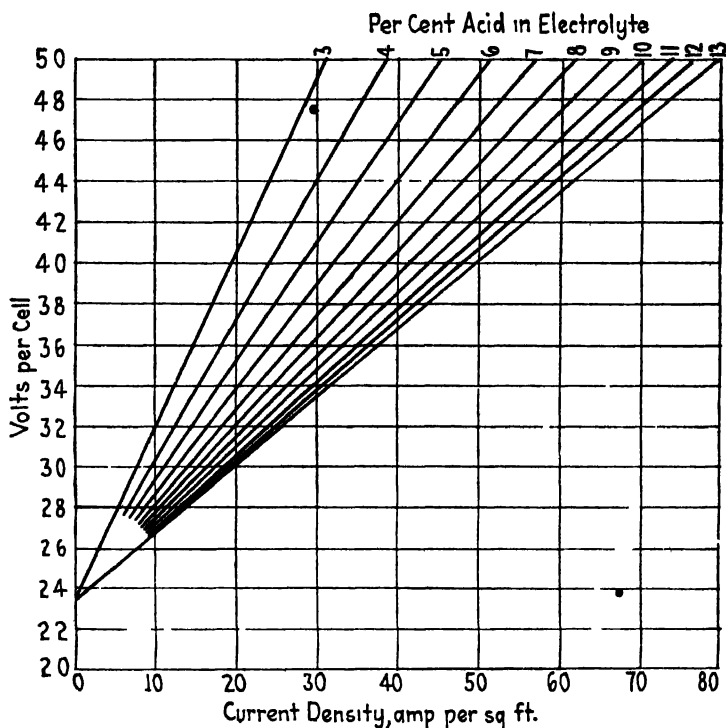


FIG. 13.—Cell resistances 2-in. electrode spacing at 35°C

can be present in solution, but little is known regarding the combined effect of two or more impurities which may be present, each in an amount less than the safe limit for that particular impurity. Results obtained by different experimenters do not agree closely in the case of some individual impurities, due probably to differences in other cell conditions, but some fairly accurate average data have been obtained for the common impurities. These will be discussed in greater detail under separate headings.

All experimenters agree that the effect of any impurity is aggravated by rise in temperature. As the time of deposition increases, the effect of any impurity becomes more pronounced. With absolutely pure solution, high ampere efficiency is obtained with 48, 72, 96 hr., or even longer periods of deposition, but in plant operation it is frequently found advisable to decrease the period to 24 hr. This is also influenced by other cell conditions, such as temperature, current density, and acidity, the most

efficient period of deposition being determined experimentally for each set of conditions and by balancing extra labor cost for more frequent stripping against power saved through improvement in ampere efficiency. The ratio of zinc to acid in solution necessary to maintain maximum ampere efficiency varies with current density, period of deposition, temperature, and purity of solution. The usual practice is to deposit from solution about two-thirds of the zinc content of the neutral solution, returning one-third to the leaching plant. If the amount deposited greatly exceeds this ratio, some loss in ampere efficiency will result.

Addition agents, such as glue, wood juice, and some of the gums, are used more or less to improve the physical condition of the zinc deposit and to aid ampere efficiency. It is not good practice to rely on these, if it is possible properly to purify solution in the leaching plant. Glue is used in almost negligible amounts at Great Falls, less than 1 oz. of glue per ton of zinc—a somewhat greater amount is used at Trail and much larger amounts are used at Hobart, Tasmania, to offset the effect of cobalt in solution.

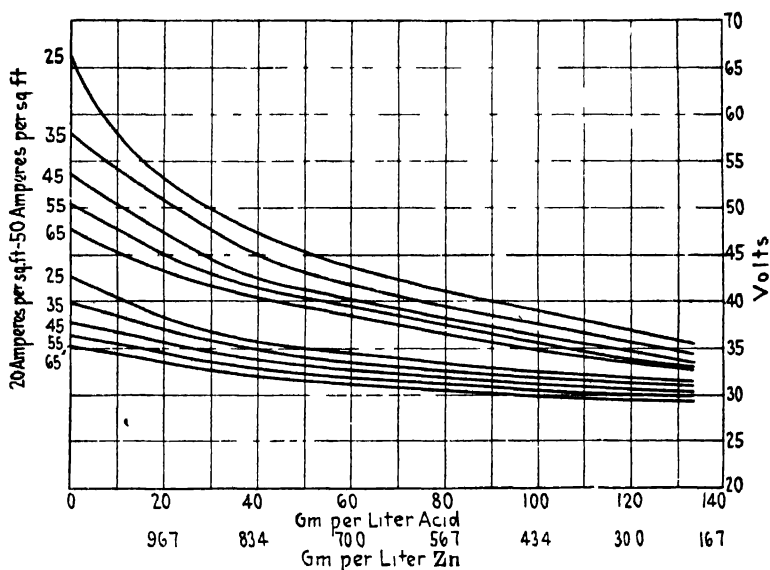


FIG. 14 Electrolyte resistance 4-in. anode spacing

**Effect of Impurities.**—In order to be certain of results obtained, it is necessary to start with an absolutely pure solution of zinc sulphate in determining the effect of single impurities, otherwise the combined effects of the impurity added and of those already present are noted. Solution prepared from the so-called c.-p. zinc salts is not of satisfactory purity for this work, without further purification. J. T. Ellsworth, at Park City, Utah, obtained what are probably the most accurate data on the effect of single impurities yet published. He prepared a solution of zinc sulphate by burning zinc of high purity to form zinc oxide and dissolving this in pure sulphuric acid, followed by agitation with zinc dust to remove traces of copper and cadmium. Definite quantities of an impurity were added to separate portions of this solution and the resulting foul solutions were electrolyzed under a standard set of conditions. The results of his work were published in Vol. 43 of the *Trans.* of the American Electrochemical Society.

The difficulty in applying any set of data on the effect of single impurities to plant operation is that a solution containing only one impurity is never obtained, and variations in cell conditions cause a variation in the effect of an impurity. The experimental data obtained have been of great value in guiding purification practice and have pointed out the most injurious impurities, and have enabled the operators to recognize the presence of some impurities from the appearance of the zinc deposit without waiting for complete analysis of solution.

*Antimony* is, undoubtedly, the most injurious impurity yet encountered in electrolytic zinc operations. If present in any amount, its effect is noticeable with high temperature and acidity. One part per million is apparent under normal cell conditions. The zinc deposit becomes spongy and dark in color; sprouts, small at the surface of zinc and large at the end, form in large numbers, and ampere efficiency is lowered markedly. As the period of deposition increases, the effects become more marked. The remedies applied are more thorough purification in the neutral leach, shortening of period of deposition, and lowering of current density to lower cell temperature.

*Arsenic*.—Alone, arsenic is much less injurious than antimony. The presence of arsenic in solution, however, is a pretty sure indication that some antimony is also present. The same purification methods used for the removal of antimony also remove arsenic, and with less difficulty. Therefore, antimony may be present in small amounts without arsenic, but arsenic is rarely present without antimony, unless the ore being treated is free of antimony. The early indications of the presence of arsenic in the zinc cell are pronounced corrugation of the surface of the zinc deposit and the absence of the usual luster of the deposit. This is followed by sprouting and serious loss in ampere efficiency.

*Copper* may be present up to 10 mg. per liter without seriously affecting ampere efficiency and, with low acid strength, may go even higher. If zinc-dust purification is carried far enough to remove cadmium sufficiently completely to produce grade A zinc, there is little danger of trouble from copper. The source of most of the copper actually present in the cells is the copper support bars and tank bars, the mist and spray from the cells slowly corroding copper over the cells and the copper sulphate so formed being washed or knocked into the cells. The amount of copper so introduced is normally insufficient materially to affect the zinc deposit, but occasional breaks in water or solution connections and roof leaks will wash a sufficient amount into a group of cells to cause violent re-solution in the cells affected. Fresh solution is run into these cells to lower the acidity and to increase the rate of flow through them, thereby quickly removing the fouled solution, and the cathodes are removed and stripped as rapidly as possible.

*Cadmium*, when present in amounts up to 0.5 g. per liter, does not lower the ampere efficiency or injure the physical condition of the zinc deposit. Small amounts of cadmium improve cell conditions according to some experimenters.

*Cobalt*.—Ten milligrams of cobalt per liter of solution will cause re-solution of the zinc deposit, unless special treatment is resorted to, but at Hobart, Tasmania, 200 mg. per liter are reported to be present without serious loss in ampere efficiency, due to the addition of large quantities of glue. In some instances, it has been necessary to use as much as 5 lb. of glue per ton of zinc produced. The action of glue is not clearly understood, but it is certain that it is of great help in reducing the injurious effect of some impurities, notably cobalt.

*Chlorine* in amounts up to 100 mg. per liter does not materially affect ampere efficiency, but corrodes the lead anodes. If the concentrate treated carries silver, the chlorine content of electrolyte will usually be insufficient to cause trouble.

*Iron* in amounts up to 0.2 to 0.3 g. per liter has been present in solution without noticeably lowering ampere efficiency, but its presence is usually an indication of

incomplete purification in the neutral leach, and arsenic or antimony, or both, are probably also present. Iron is commonly present in solution up to 0.03 g per liter. Undoubtedly, much of the trouble assigned to iron has been caused by associated impurities.

**Manganese**—Up to 3 or 4 g per liter, manganese is not seriously injurious. Part of the manganese in solution is precipitated as  $MnO_2$  at the anode and forms

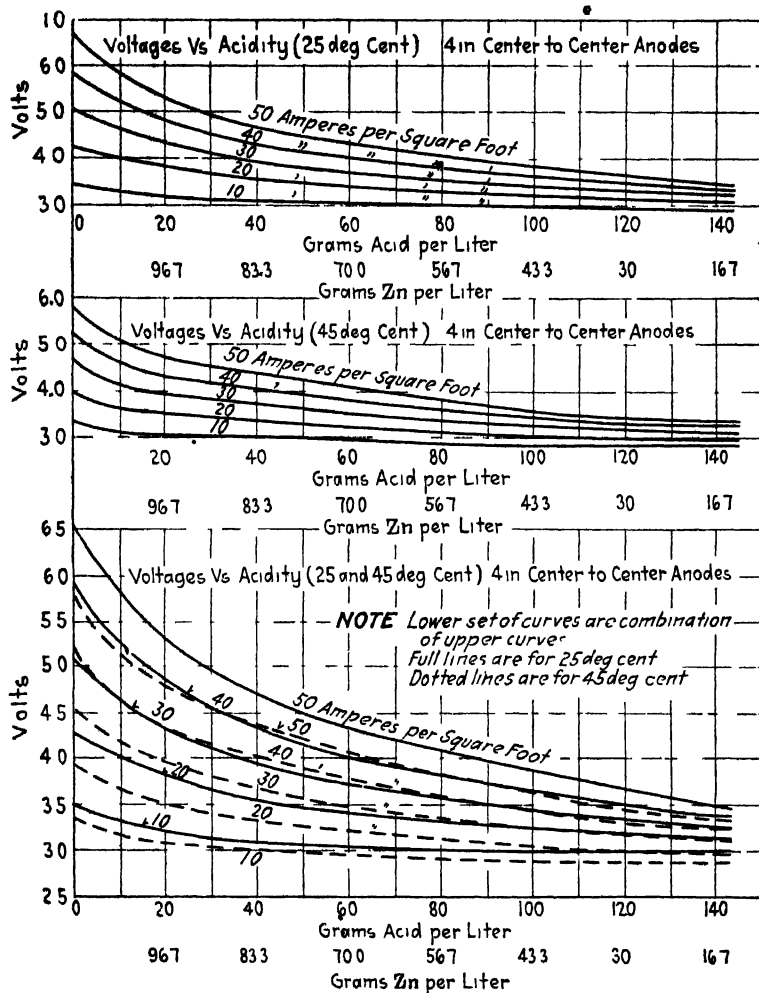


FIG. 15. Electrolyte resistance.

a protective coating for the anode. The amount that adheres to the anode seems to be dependent upon temperature and acidity, and possibly current density. Low acidity, temperature and current density cause a heavy anode coating. Some experimenters claim that manganese aggravates the effect of antimony; others claim that it acts as a deterrent on the action of copper. It is doubtful that it has any great influence on current efficiency, one way or the other, until it is present in

amounts of 3 g. per liter or over. Ellsworth found it to be seriously injurious in larger amounts.

*Nickel* seems to have less effect than cobalt, but is classed as one of the highly undesirable impurities. Not much work has been done to determine the effect of nickel, as it is not a commonly found impurity in zinc-plant solutions.

*Sodium, Potassium, Magnesium, Aluminum, Iame, etc.*—In amounts usually found in solution, these impurities are not known materially to affect either ampere efficiency or physical condition of deposit. After 10 years' operation of one plant, no appreciable increase in the amount of any of these impurities has been noticed.

**Current Density.**—Local conditions determine the most economical current density. The leaching division, almost as much as the electrolyzing division, is affected in design and operation by the current density employed. A wide range of current density may be used, if all conditions are properly adjusted, but, after careful investigation of all factors entering into the choice for large-scale operation, the larger companies have decided on a range of from 20 to 30 amp. per square foot of cathode surface as the most economical and satisfactory density. Going much above the 30 amp. per square foot requires special provision for cooling of cells and requires higher acidity to keep down power consumption, which, in turn, requires higher zinc content in cell feed, and is reflected in complications in the leaching division. Below 20 amp. per square foot the first cost of plant is high and the zinc deposit is not so firm as with higher density.

Increase in current density is always attended by increase in power input to cells, due to higher voltage. By increasing the acidity, and decreasing the spacing of electrodes, resistance in the cell is decreased, and increases in density are not accompanied by as great increases in voltage as with lower acid and standard spacing of 4 in. from center of anode to center of anode. Above 12 to 13 per cent acid, the zinc content of cell feed must be higher than the saturation point of zinc sulphate solution at ordinary temperatures, and the density of solution is increased sufficiently to hinder settling in the thickeners. Washing the residue is made more difficult and the probable loss of water-soluble zinc is increased. Cutting down on the spacing of electrodes increases the number of short circuits and adds to the cost of inspection and stripping. The effects of increasing current density under varying cell conditions are shown diagrammatically by Figs. 13, 14, 15, and 16.

If current density is to be increased beyond the point where cooling equipment placed in the cells is sufficient properly to cool the electrolyte and where supersaturated zinc sulphate solution is required to maintain sufficiently high acidity, a decided increase in current density, up to 100 amp. per square foot or higher, may as well be made. Large-scale tests have been made using current density of from 100 to 120 amp. per square foot with 25 to 30 per cent  $\text{H}_2\text{SO}_4$  in the electrolyte. The only authentic published data on this work showed that, even with this acidity, the power requirements were about 1.77 kw.-hr. per pound of zinc for a test plant, as compared with normal operation requirement of 1.5 kw.-hr. per pound for the large plants using about 30 amp. per square foot and 10 to 12 per cent  $\text{H}_2\text{SO}_4$ , or an increase of nearly 20 per cent in power required. This amounts to about \$2.75 per ton of zinc with power at \$30 per horsepower-year, or \$275 per day, or \$100,000 per year for a plant producing 100 tons of zinc per day. An elaborate solution circulating system was required to maintain a sufficiently high rate of flow through the cells, by returning about six-sevenths of the spent electrolyte to be mixed with fresh solution fed to the cells. This mixture must be cooled before being fed into the cells and only one cell can be placed in series, as regards solution flow, to avoid overheating in the cells. Circulating



and cooling equipment must be acidproof and a very large proportion of tank-room space must be put into aisles and working spaces. Special types of anodes and special equipment for holding cathodes evenly spaced from anodes is required. Also, 20 per cent more power equipment is required than for a plant of equal capacity operating at 30 amp. per square foot. Mechanical agitators are required for leaching, to conserve heat, and pressure filters for filtration of leached pulp. Both leaching and filtration are conducted in batches and require close personal supervision to avoid excessive loss of zinc in the residue. All tanks and equipment in the leaching division require heating coils or equipment of some kind to prevent cooling of solution with crystallization of zinc sulphate. No commercial plant has been built to employ the higher current densities, making such items as first cost of plant and operating costs nothing more than estimates. A careful analysis of all the factors involved, considering the type of equipment and construction materials required, does not indicate any material saving in first cost of plant, but does indicate a material increase in operating and repair costs, especially in power cost. Operation of a high-density plant can not be made so nearly "foolproof" as that of a low-density plant, and closer personal supervision is required throughout to insure equally good results. High densities, as applied up to the present time, show little promise of supplanting low density except in localities having exceptionally low power cost, and other unusual conditions which might justify such an installation.

**Period of Deposition.**—Shortening the period of deposition nearly always results in some increase in ampere efficiency. When some impurity is present, or if the temperature of the electrolyte is higher than normal—above 40°C.—the effect of variation in time of deposition is more pronounced than if the electrolyte is cool and of high purity. It is somewhat generally supposed that the use of high current density lessens the effect of impurities in solution, but the real reason is probably not so much that high current density lessens the effect of impurities, as that shorter periods of deposition are used with high density. As the period of deposition is lengthened, the deposit gradually becomes rougher on the surface and tends to spring loose from the surface of the aluminum cathode. With 30 amp. per square foot and less than 45°C. temperature in the cell, the usual period of deposition is 48 hr.; with higher temperature it may be decreased to 24 hr. with sufficient increase in ampere efficiency to offset increased stripping cost. With lower density—20 to 25 amp. per square foot—and lower temperature in the cell—40°C. or less—the period may be lengthened to 72, or even 96 hr., without serious loss in ampere efficiency.

**Miscellaneous Tank-room Notes.**—Rotating cathodes have been tried in place of stationary cathodes, with the purpose of producing a heavier and smoother deposit, but have been discarded from the plants in which they were installed. Approximately only one-third of the area of the cathode was immersed in the electrolyte, the remainder being subject to re-solution of the zinc deposit by the adhering electrolyte. With discs of the size required, warping took place and resulted in the edge of the cathode coming in contact with the anode. Cathode contacts gave trouble and the shaft carrying the cathode discs was corroded by the electrolyte carried up by the discs. Stripping the deposit was a slow and expensive operation, and when impure solution reached the cells, it was impossible to remove the cathodes and strip them as rapidly as was necessary. Some very smooth and heavy zinc deposits were obtained in the test plant where this type of cathode was first used, but its practical application was not so successful.

Purity of zinc produced can be controlled partly by varying cell conditions and partly by control of the zinc-dust purification. The cadmium content of the zinc deposit is altogether dependent upon the purity of the electrolyte. Lead in electrolytic zinc undoubtedly comes from the anodes, the amount being largely dependent upon cell conditions. High temperature and high acidity give high lead content in the deposit, probably on account of imperfect coating of the anodes with manganese dioxide under these conditions, allowing particles of lead to be carried over and held mechani-

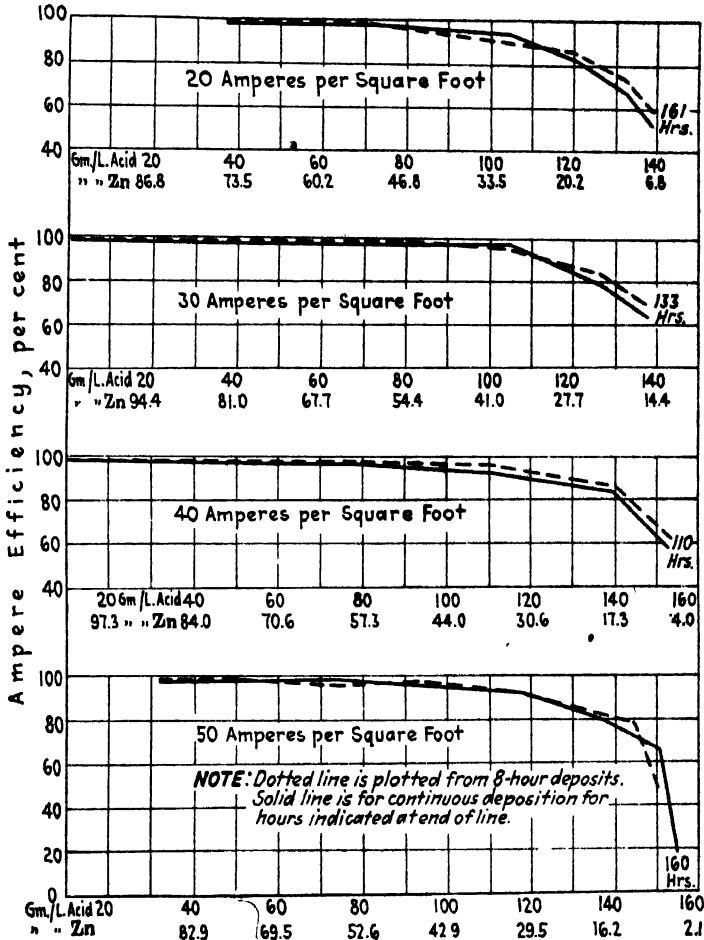


FIG. 16.—Effect of time of deposition and ratio of zinc to acid on ampere efficiency.

cally by the cathode deposit. Rough deposits produced by long period of deposition carry more lead than smoother deposits. With 30 amp. per square foot current density, 10 per cent acid, and 50°C. temperature, and a 48-hr. period of deposition, zinc containing 0.10 per cent lead was produced. The period of deposition was decreased to 24 hr., with other conditions the same, and the lead content dropped to 0.07 per cent. The rate of corrosion of the anodes does not seem to affect the lead content of zinc deposit. One plant had serious trouble from anode corrosion, on account of

chlorides in solution, but produced zinc of high purity and maintained high ampere efficiency. Low temperature has greater effect in reducing lead content than any other factor, and where both temperature and acidity have been reduced, zinc with 0.01 to 0.015 per cent lead has been produced at 30-amp. density. Iron never goes above 0.002 to 0.003 per cent in slabs produced, and this is probably derived more from melting and casting equipment than from cathodes.

The amount of solution held by the zinc deposit is so small, and its zinc content is so low, that washing of the sheets is not necessary. An average deposit, as sent to the casting plant, will contain about 0.25 per cent moisture.

Starting sheets of zinc have been tried in place of aluminum depositing blanks, but have never proved a success. Thin deposits of zinc tear easily and, when dried, become quite brittle, making the producing, storing, and handling of such sheets a difficult problem. Contacts between starting sheets and supporting bars have not been satisfactory, and the sheets tend to redissolve at the solution line, especially if the electrolyte becomes slightly impure, causing sheets to fall into the tanks. The use of depositing blanks leaves little to be desired and not sufficient trouble has been had with the blanks to furnish any incentive to work out the starting-sheet problems. There would be some saving in cost of aluminum and some advantages in having a heavier deposit to be melted, but the experiences with starting sheets have not been particularly encouraging.

No oil or other preparation is necessary, except in rare instances, to be applied to the surface of aluminum starting blanks in order to strip the zinc deposit without difficulty. One or two periods of trouble with sticking of deposits have been encountered, but they have not been of long duration. Wiping the surface of the blank with gasoline before replacing in the cell will prevent any tendency toward sticking, if the surface of the blank is not pitted. Some aluminum sheets develop scaly surfaces and the pitted spots, so formed, cause sticking of the deposit. The best remedy for these is to scrap them.

Aluminum sheets corrode most rapidly at the solution line, and between that point and the support bar, due to spray of electrolyte from the cells and corrosion by copper sulphate from support bars. That portion of the sheet below the solution level is protected by the zinc deposit and is usually nearly untouched when the top is corroded through. Welding a strip to the top of old plates has been tried and a good weld can be made, but the plates, so repaired, will corrode rapidly at the point of welding. A plant having five units in the tank room might advantageously design two units of the five to use smaller electrodes than the remaining three units and supply cathodes to these two units from the scrap resulting from the three units, thereby getting nearly double the period of use from the aluminum purchased. The actual loss in weight of aluminum, when a sheet is discarded, is not great, and the actual consumption of aluminum per ton of zinc would be a very small item in the cost of producing zinc, but the difference between cost of new sheets and their scrap value is so great that the loss on the unused portion of the sheet makes the cost for aluminum about 2 per cent of the entire operating expenses.

Good ventilation is essential to satisfactory operation of the tankroom. Some mist and vapor are always present in the atmosphere and, if allowed to condense, contacts are corroded and the building roof structure is attacked. The fact that the mist contains sulphuric acid and zinc sulphate adds to the necessity of good ventilation from the standpoint of working conditions. These chemicals will attack the nasal passages, causing ulcers, unless some form of respirator is used. Ordinary cheese cloth, with several layers folded together, makes a very satisfactory covering for the nose and mouth and absolutely prevents any ill effects on the workmen. In summer, ventilation is necessary to keep down the temperature of the atmosphere in the

tank room. Part of the heat generated in the cells is radiated, and the large area of solution exposed rapidly heats the entire building, if good circulation is not maintained.

When it becomes necessary to discard solution, due to the overproduction of sulphate in roasting, the solution to be discarded is put through a group of cells maintaining a higher than normal rate of flow to avoid overheating and the zinc content depleted to less than 10 g. per liter. The resulting ampere efficiency will be lower than normal by 10 to 20 per cent, but the voltage on these cells is also below normal, so the actual loss in power is not of so much consequence.

**Melting and Casting.**—Electrolytic zinc, as cathode sheets, has a very limited market and, for most purposes, must be melted and cast into slabs. Melting must be done under carefully controlled conditions to avoid formation of an excessive amount of dross composed chiefly of zinc oxide. Casting of the molten zinc into slabs is a simple operation and can be done very cheaply. The total cost of melting, casting, handling dross, and loading slabs for shipment amounts to only about 8 per cent of the total zinc production operating expenses, when hand labor is used for casting and loading.

A reverberatory type of furnace is used for the melting operation, the depth of bath being greater than is customary for similar furnaces for most other metals, varying from 30 to 36 in., depending upon the area exposed for heating the bath. With a depth of bath of 30 in., the hearth should be about 15 ft. wide by 20 ft. long. A furnace designed to derive its heat through the bath from underneath would be better suited to the purpose than one heated through the surface of the bath, because as much melting as possible is done under the surface of the bath and, in order to drive the necessary heat into the bath, the temperature in the furnace is carried too high to avoid burning some zinc to zinc oxide.

To prevent loss of zinc through the furnace bottom, a steel pan is placed on concrete piers, to allow circulation of air under the furnace bottom, and the brick hearth is built inside of the pan. Common brick may be used for the bottom and hearth, and fire brick above the metal line and in the roof. A charging hole, large enough to permit passage of a cathode sheet, is built into the roof, and muffles, from which zinc is ladled to be cast, are built into the end of the furnace. These muffles are open on the bottom, and the sides extend below the surface of the bath to prevent dross from getting into the casting ladles and to exclude air from the furnace. Doors are provided along the sides of the furnace, just above the metal line, for rabbling and skimming dross.

Casting is usually done by hand, using ladles carried from a trolley running on an overhead I-beam, each ladle holding about 200 lb. of zinc. Molds are placed in a straight line under the I-beam. The molds are made of cast iron, and produce a slab weighing from 50 to 60 lb.

Dross is removed from furnace in wheelbarrows or concrete buggies and is delivered into a heated steel drum which, revolving in one direction, mixes the charge thoroughly, and when revolving in the opposite direction will empty itself. A drain placed in one end of the drum allows molten zinc, separated from the dross, to be removed. A separate furnace may be provided to receive the dross and, by continued heating, drive out most of the chlorine, giving a product which may be returned to the leaching system.

**Furnace Operation.**—Any fuel may be used with which a reasonable control of the furnace atmosphere and temperature may be had. In order of preference, fuels are gas, oil, and coal. If lump coal is used, the fire box should be deep enough to give a partial effect of a gas producer. A distinctly reducing atmosphere

should be maintained in the furnace to avoid burning the zinc, and the gas temperature should be kept below 600°C., preferably around 550°C.

Cathode sheets are charged into the bath of molten zinc in bundles weighing about a ton each, using some system, such as rollers, for sliding the bundle into the furnace with the least possible admission of air. Charging may be done through either the side or the roof of the furnace. As the bundle falls into the bath, the individual sheets, each weighing 15 to 20 lb., spread, allowing molten zinc to pass around each sheet. In order to spread the charge as much as possible, more than one charging space may be provided, if the furnace is large enough to require it. The total charge should pass into the bath and be out of contact with the furnace gases, melting taking place under the surface of the bath and receiving the necessary heat through the layer of dross on the bath. Charging and casting are carried on simultaneously, holding the level of the bath about constant.

Some air is admitted with each charge of sheets and each sheet has a thin film of zinc sulphate on its surface. The greater the amount of "sprouting" on the sheets and the greater the porosity of the sheets, as when produced from impure solution, the greater the amount of air carried into the bath and the greater the amount of surface film per pound of zinc. The zinc oxide formed in the furnace and the zinc sulphate from the surface of the sheets form a "dross," which rises to the surface of the bath of molten zinc and holds a high percentage of metallic zinc, forming a blanket of mushy material through which succeeding charges must pass. After about 16 hr. charging, the furnace is allowed to cool down and this blanket is worked or rabbled to separate as much of its metallic content as possible, the metallic zinc going into the bath, leaving the mixture of oxide and sulphate on the surface. In order to get a good separation of oxide and metallic zinc, sal ammoniac is worked into the rich dross, causing the particles of metallics to brighten and coalesce. The addition of sal ammoniac generates heat and some zinc is burned during the rabbling period, as it is necessary to have the side doors open to admit the rabbles, also admitting air. After being thoroughly worked in this manner, the remaining dross is raked out through the doors and transferred to the dross drum or furnace, where more sal ammoniac is added and the resulting metallic zinc is allowed to drain out of the "dry" dross. A fairly complete separation is thus obtained, producing a dross containing about 82 per cent zinc. From 3 to 5 per cent of the weight of cathode sheets charged goes into dross, the amount depending upon the physical condition of the sheets, furnace operation, and the thoroughness with which the dross is treated for the recovery of metallic zinc. Less than 4 per cent dross is considered good work for average cathode sheets. Normal consumption of sal ammoniac is about 1 lb. per ton of cathodes melted. Approximately 20 tons of cathodes can be melted per ton of coal burned. In addition to coal requirements, some oil is burned in the casting muffles, and oil is burned around the dross-treatment drum, the total requirement being from 1 to 1½ gal. per ton of zinc.

Dross is a desirable source of zinc for lithopone and for zinc chloride, much of it having been used for these purposes. It is also a desirable material for some retort zinc smelters, requiring no roasting and enriching the lower zinc materials treated. Its chloride content is the only objection to returning it to the leaching division. Roasting at 400 to 500°C. will remove the chlorine content sufficiently to permit retreatment in the leaching division, if calcine being treated contains some soluble silver. If dross is retreated, roasting, leaching, purification of solution, electrolysis of solution, and melting of the resulting cathode sheets must be charged against zinc recovered. The location of the zinc plant with respect to market for dross and the cost of retreatment are the usual determining factors in deciding the best method of disposal.

**Zinc Dust.**—Zinc dust for copper-cadmium purification is made by atomization of molten zinc with compressed air, using a nozzle made from an ordinary

pipe cap by boring holes or sawing a slot of the proper form. Molten zinc is transferred from the melting furnaces to a graphite crucible or pot provided with suitable heating arrangement to keep zinc molten. Graphite plugs having  $\frac{1}{8}$ -in. holes bored through the center are fastened in the bottom of the crucible, and the nozzles are so placed that the stream of compressed air issuing from the nozzle catches the stream of molten zinc, atomizing it and blowing it into a settling chamber provided with some means of escape for air without loss of zinc dust. The particles of dust are chilled so rapidly that practically no oxidation takes place. Fineness of dust is controlled by air pressure, size of stream of zinc, and design and location of nozzle with respect to stream of zinc.

The outline formed by the holes in the nozzle, or the form of the slot, is of great importance in determining the efficiency of atomization. A V, with rounded bottom,

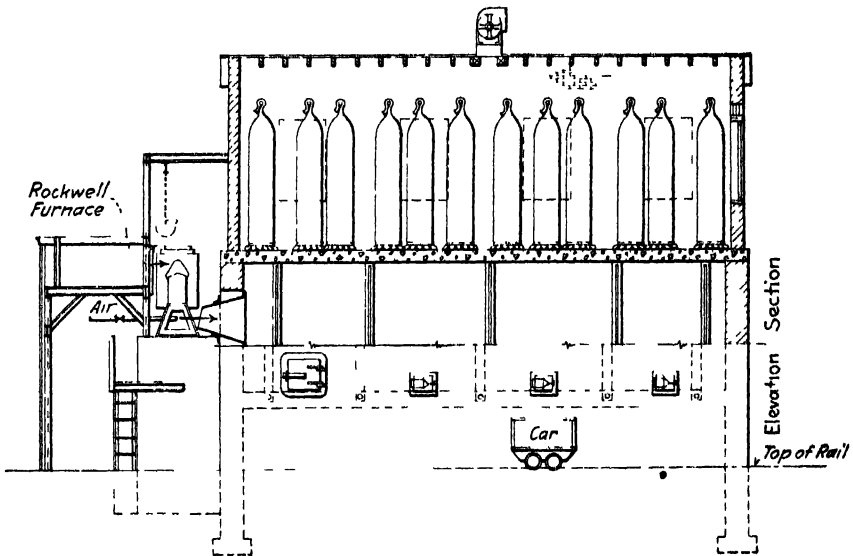


FIG. 17.—Zinc-dust plant.

or a crescent-shaped air jet are the most efficient. The sides of the jet should close just beyond the point where the stream of zinc strikes it, to prevent spraying. The bottom of the jet should be heavier than the sides. The stream of zinc should strike the air jet just back of the point where the sides of the jet come together; if too far back of this point, some zinc will be carried up and out, escaping before being completely atomized; if too far ahead of this point, the zinc stream will not be entrapped in the air jet.

High air pressure gives finer dust, but 75-lb. pressure will give a product most of which is finer than 100 mesh. Air supply must be well trapped to remove any oil carried over from the compressor, otherwise an explosion may occur in the dust-collecting system. Open flames should be kept away from the dust plant, the fine dust being highly inflammable.

If classification is desired, sufficient air is drawn through the chamber into which the dust is blown, to carry out the finer dust, and is passed through a suitable collecting equipment. If no classification is desired, the chamber is vented through bags or other filtering equipment located over the chamber and discharging into it.

## GENERAL PLANT DATA

**Labor.**—The total labor required for operation and maintenance, including everything from the unloading of the concentrate to the shipping of the finished zinc, will vary from 1.5 to 2.0 men per ton of zinc produced, depending upon the capacity of plant and the grade of concentrate treated. Low-grade concentrate requires more men per ton of zinc produced in the roasting and leaching divisions than high-zinc concentrate. Increasing the capacity of a plant decreases the number of men required per ton of zinc. A high percentage of the labor required is what is usually termed unskilled labor. Working conditions are such as to attract a good class of labor.

**Power.**—The actual power required for deposition of zinc at 30 amp. per square foot will average about 1.5 kw.-hr. direct current per pound of zinc. Assuming 93 per cent conversion efficiency from alternating current to direct current, approximately 1.6 kw.-hr. alternating current will be required per pound of zinc, or 3,200 kw.-hr. per ton of zinc. Auxiliary power for roasters, leaching plant, casting, compressed air, etc. varies in its relation to power for cells with the size of plant and the grade of concentrate being treated. For a plant producing 100 tons of zinc per day from 40 per cent zinc concentrate, auxiliary power amounts to approximately 10 per cent of total power; as the capacity of the plant is increased the proportion of auxiliary power is decreased. With 10 per cent for auxiliary power, the total power requirement for a 100-ton plant will be 3560 kw.-hr. per ton of zinc, or approximately 15,000 kw. total requirement. Decreasing the current density to 25 amp. per square foot will result in decreasing the above figure about 5 per cent.

For a 48-hr. period of deposition, 87 per cent ampere efficiency is considered a good average at 30 amp. per square foot. At 25 amp. per square foot, ampere efficiency will normally be higher by 3 to 5 per cent, due to better cooling of the cells.

**Auxiliary Equipment.**—Leaching in Pachucas requires from 125 to 150 cu. ft. of free air per minute, per tank. This air is supplied at from 20 to 30 lb. pressure. Some air is required for the agitation of pulp in filters, opening up thickener spigot lines, and for similar miscellaneous purposes, higher pressure than 30 lb. being desirable for these uses. Zinc-dust manufacture requires at least 75 lb. pressure, the volume of air depending upon the number of nozzles and the size of the stream being atomized. For all purposes, an average 100-ton plant should have at least 1,000 cu. ft. of high-pressure capacity.

The only steam required, except for heating buildings, is for heating water to wash the residue, heating the solution for the precipitation of cadmium recovered from purification residue, heating the spent electrolyte used to dissolve iron for neutral leach, change house, and office use, and a few minor miscellaneous uses. The amount required for heating buildings will depend on climatic conditions and the type of building construction. Some heat is generated in the leaching tanks, the temperature averaging 50°C. or higher, and the large area exposed by the surface of the thickeners allows much of this heat to be radiated, thereby reducing the amount of steam heating required in the leaching division. A similar condition exists in the electrolyzing division, as regards generation of heat, but, on account of the ventilation required, not so much can be conserved as in the leaching division. No steam heat is required in the melting and casting division beyond that needed to keep air and water lines from freezing and for heating oil.

Water is required in increasingly large quantities, as current density is increased, for cooling of cells. If the plant is so arranged as to permit of its proper distribution, the water used for cooling of cells may be used again for all other requirements of the plant, with the possible exception of cooling water for transformers. The cell requirement, 6 to 8 gal. per minute per ton of zinc daily output, is more than sufficient in volume for the other requirements and is not contaminated in passing through the cooling coils.

A small foundry for making copper, bronze, and lead castings for spare parts for equipment in contact with acid- or copper-bearing solution is almost a necessary adjunct to an electrolytic-zinc plant and will prove to be a highly profitable investment. Carpenter, pipe, boiler, blacksmith, electric, and machine shops are needed to care for the regular maintenance work.

**First Cost of Plant.**—Including all auxiliary departments, water system, tramming system, bins, etc., the first cost will vary from \$25,000 to \$40,000 per ton of daily zinc capacity, depending upon size of plant, type of construction, grade of concentrate treated, cost of labor and supplies, and location of plant. Thus, a very large plant, 200 to 250 tons of zinc per day, built under the most favorable conditions, would cost \$25,000 per ton of daily zinc capacity. A plant of half of the capacity, under the same conditions, would cost from \$30,000 to \$35,000 per ton. Power-conversion equipment and motors make up the largest single item of cost. The second largest item is made up of electrolytic-cell equipment, such as aluminum cathodes, lead anodes, cooling coils, tank linings, copper bus bars, tank bars, conductor bars, and other lead and copper items. Much of the leaching plant equipment is lead, bronze, or copper. Roasting and leaching equipment is practically all of standard design for use in other industries, giving it a greater salvage value than if of special design.

The first cost of an electrolytic-zinc plant depends less upon the grade of material being handled than does a retort plant, as the electrolyzing division and the melting and casting division are altogether dependent upon the amount of zinc produced, regardless of source, and much of the leaching-division equipment is dependent upon the volume of solution to be handled, and, therefore, on zinc output. The roasting equipment necessary is largely dependent upon the grade of concentrate, as is also, to a large extent, some of the leaching-division equipment. More low-zinc concentrate can be roasted per furnace than high-zinc concentrate, but a greater proportion of the zinc in the high-zinc concentrate is rendered soluble, so the roasting equipment required for a given zinc production is roughly inversely proportional to the grade of zinc concentrate treated. The first cost of plant is, therefore, less the higher the grade of concentrate treated.

**Recoveries.**—Total losses in the roasting division should amount to less than 2 per cent, the chief loss being dust loss. Cottrell treaters or settling chambers will recover most of the dust carried from the furnace by the furnace gases. The amount carried out of the furnace is necessarily high when roasting flotation concentrate in a multiple-hearth furnace, but is only a mechanical loss and is common to any process using similar equipment for this class of feed. Other sources of loss in the roaster division are handling losses incurred in screening and cooling calcine and in crushing oversize calcine preparatory to returning it for roasting.

Leaching-plant residue contains zinc sulphide remaining unroasted in calcine, zinc ferrate insoluble in leaching solution, some zinc oxide not dissolved in leaching, and



any zinc sulphate not removed by washing residue with water. The total loss of zinc as residue is the largest single loss of the electrolytic process and may amount to as much as 20 per cent of the total zinc with particularly unfavorable zinc ore, such as marmatite, which is a fused mixture of zinc and iron sulphides. Loss as ferrate is usually the main part of the residue loss, but in the case of very pure ores, such as Joplin ores, the loss as sulphide may exceed the ferrate loss. Any unroasted zinc sulphide carries approximately twice as much zinc as sulphur. Therefore 0.2 per cent sulphide sulphur in calcine, which may be taken as good average roasting practice, will mean a loss of 0.4 per cent zinc, equivalent to 1 per cent of total zinc in a 40 per cent zinc concentrate. Concentrate containing much iron will produce a correspondingly high percentage of residue with a large loss of zinc as ferrate. As pointed

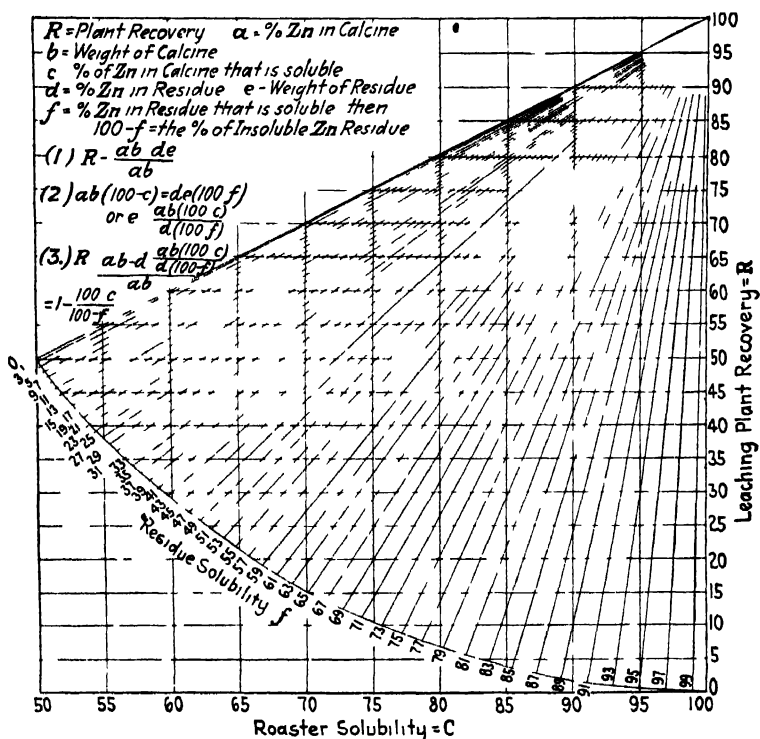


FIG. 18. Graphic zinc-recovery formula (based on fact that insoluble zinc in calcine equals insoluble zinc in residue)

out under roasting, the amount of ferrate formed cannot be definitely predicted from an analysis of the concentrate, as the intimacy of contact between particles of zinc and iron influences the completeness of combination, but it can be assumed for general purposes that, as the iron content of concentrate increases, the amount of ferrate loss in residue will increase. The real measure of the efficiency of leaching is shown by the amount of undissolved zinc oxide remaining in the residue, good operating efficiency being a reduction of such zinc in the residue to less than 10 per cent of the total zinc in the residue. When treating 55 per cent zinc concentrate, the total zinc in the residue will be about 6 per cent of the zinc in the concentrate, of this amount, 8 per cent, or 0.5 per cent of the zinc in the concentrate, should be present in

the residue as zinc oxide. Approximately twice as much zinc as zinc sulphate will remain in the residue as is present as zinc oxide, that is, from 10 to 20 per cent of the total in the residue, or approximately 1 per cent of the zinc in the original concentrate. To sum up residue loss from a 55 per cent zinc concentrate; 0.2 per cent sulphur unroasted causes 0.7 per cent loss; undissolved zinc oxide causes 0.5 per cent loss; unwashed zinc sulphate causes 1 per cent loss; and ferrate causes approximately 3.8 per cent loss, or a total of 6 per cent. As the zinc content of the concentrate decreases, with a corresponding increase in iron content, the percentage loss from sulphide and ferrate will increase and the percentage loss as zinc oxide and zinc sulphate will decrease. With a 40 per cent zinc concentrate, the residue loss will amount to about 12 per cent of the total zinc.

Figure 17 gives a formula for determining leaching recovery, or recovery from calcine to residue, and is based on the fact that the amount of zinc in a definite amount of calcine that is insoluble in 1 per cent  $H_2SO_4$  equals the amount of such insoluble zinc in residue produced from this calcine. The recovery calculated from this formula does not include any loss in purification residue.

The amount of the purification residue produced and its zinc content depend upon the amount of copper and cadmium dissolved, therefore on the amount of zinc dust used for purification of solution. Basic sulphate precipitated from solution and solids overflowing the neutral thickeners make the zinc content of this residue approximately equal to the amount of zinc dust used. Retreatment for recovery of zinc and separation of copper and cadmium will recover from 50 to 75 per cent of the zinc contained. An average figure for the net loss of zinc from this source would be about 30 per cent of the zinc dust used.

There is no loss of zinc in the electrolytic division, unless acid is discarded. As this is an intermittent proposition and the zinc is depleted from solution to 1 per cent or less, no estimate can be made of the loss from this source for any given ore, but it is certain not to be of serious consequence, if roasting is properly controlled.

Some zinc is lost from the melting-furnace operation, amounting normally to about 0.25 per cent of the total zinc.

Depending upon the arrangement of plant divisions, as affecting the handling of calcine from roasters to leaching tanks, and upon provisions for handling occasional spills of solution, there is some handling loss of calcine and solution, usually not much in amount, but sufficiently large to require making some allowance in estimating probable recovery. The sum of all such losses in leaching and electrolyzing divisions will vary from 0.5 to 1.5 per cent of the total zinc.

Starting with a flotation zinc concentrate containing 55 per cent zinc, 0.6 per cent copper, and 2 per cent iron, expected losses would be about as follows: roasting, 2.0 per cent; leaching-plant residue, 6 per cent; purification residue 0.75 per cent; melting furnace, 0.25 per cent; general handling, 1 per cent, total, 10 per cent, or a recovery of 90 per cent from concentrate to zinc.

**By-products.**—The location of the plant with respect to markets for the by-products limits the value and the production of these materials. Common by-products, which may be produced in connection with regular plant operation, are sulphuric acid, zinc dust, zinc oxide, lithopone, zinc salts, cadmium, and cadmium salts.

Sulphuric acid is being produced from the roaster gas of one electrolytic zinc plant and, where a satisfactory market exists, there is no reason why acid cannot be produced from the roaster gas from an electrolytic plant as well as from the gas from roasters in a retort plant, except when a high percentage of iron is present in the concentrate. With a high iron feed, close temperature control is required and the

Lead is deposited as a sponge, containing about 80 per cent lead when dried, and which oxidizes rapidly in contact with air and melts with the formation of a large amount of dross. At the present stage of development, the process is really one of concentration rather than of direct reduction of lead. However, the low cost of operation and of equipment required and the high recovery of lead obtained make the process very attractive for this class of material. Large-scale tests have been conducted at Trail, and at Great Falls, and the results of a large amount of work done by the Bureau of Mines at Salt Lake City are published in *Bull.* 157 of the Bureau of Mines, "Innovations in the Metallurgy of Lead" by Dorsey A. Lyon and Oliver C. Ralston.

Residue in class 3 is usually a straight lead-smelting problem. Low recovery of copper, silver, and gold eliminates the brine-leaching method, except under particularly unfavorable conditions for lead blast-furnace smelting. Large-scale tests are being conducted by the Bunker Hill & Sullivan Mining & Concentrating Co., at Kellogg, Idaho, with a wet method that may prove to be applicable to this class of material, in which leaching is done with a brine solution, saturated with chlorine gas. Graphite anodes and rotating sheet-steel cathodes are used, lead being recovered in the form of pellets which are readily melted without much dross loss. High recovery of lead, silver, and gold is claimed, and it is also claimed that the precipitation of gold and silver may be so controlled that part of the lead produced is sufficiently pure for marketing without further refining.

Some residue that will fall into class 3 contains hardly enough lead to pay freight and cost of treatment at a lead smelter, but does contain enough silver, gold, and copper to make it a valuable product. Such a residue may be smelted in a reverberatory furnace, with suitable fluxes and reducing material, producing copper matte containing most of the silver and gold, and fume containing a high percentage of the lead. The matte is treated in a converter to recover copper, gold, and silver as blister copper and the fume, carrying 45 to 50 per cent lead, is shipped to a lead smelter. Some lead is reduced to metallic lead and is tapped with matte, or goes into the furnace bottom. That going out with matte may be either separated from matte, if in sufficient amount, or may be driven into fume from the converter. Zinc is largely absorbed by the reverberatory slag, but some goes off as fume with the lead. Copper concentrate, or other sulphur-bearing material for matte formation, limestone, crushed coal, and siliceous ore, if silica is needed, are mixed with the residue to make up the reverberatory charge. Slag containing 30 per cent  $\text{SiO}_2$ , 30 per cent  $\text{FeO}$ , and 16 per cent  $\text{CaO}$  has been found to carry the least lead and copper and the most zinc of any of a series covering a wide variation of analyses. Such a slag will normally contain less than 2 per cent lead and over 12 per cent  $\text{ZnO}$  when treating residue containing 12 per cent lead and 12 per cent zinc. About 4 per cent of the weight of the residue of screened coal is required.

Residue in class 4 may be treated in a reverberatory furnace, as just described, or may be treated in a copper blast furnace or reverberatory, if it is not high enough in lead to justify the formation of a type of slag to insure its elimination and the filtration of the gases through bags to recover the fume.

A combination reverberatory and lead blast-furnace method of treatment is especially adapted to the treatment of residue containing some copper, high zinc, and not enough lead to make direct lead blast-furnace treatment economically feasible. Part of the residue is smelted in a reverberatory furnace, thereby eliminating copper, and most of the zinc, in matte and slag, and producing fume high in lead and low in zinc and copper. This fume is mixed with the remaining residue to make the blast-furnace charge, thereby reducing the amount of zinc to be slagged in the blast furnace, reducing the amount of matte formed, and giving a greater lead fall.

Before residue can be treated in a blast furnace, some form of agglomeration must be resorted to, in order to keep down dusting losses. A fair sinter may be made by

mixing the residue with foul slag and coal and putting the mixture over a Dwight-Lloyd machine, or it may be briquetted, without any addition of other material, to form briquettes sufficiently hard to handle without producing much fines. Addition of fume to the residue hardens the briquettes, being an added advantage of the combination reverberatory and blast-furnace method. Partly dried residue is fed into a pug mill, where just the right amount of water is added, and this product is put through an auger brick machine. The resulting ribbon is cut into blocks of suitable size, and dried. Zinc sulphate and the gelatinous material contained in the residue have sufficient binding properties to make a good, hard briquette.

It is possible to eliminate zinc, as well as lead fume, in the reverberatory furnace, but the cost of treatment and the cost of purification of solution produced from the fume more than offset the value of zinc recovered. Arsenic, antimony, etc., contained in the furnace charge are concentrated in the fume and are dissolved in the leaching operation, giving a solution so impure that special methods must be employed to prepare it for electrolysis. Slag having a high formation temperature, and a high percentage of reducing fuel in the charge, are required to insure good reduction and elimination of zinc, thereby decreasing tonnage smelted and increasing the operating cost. Fuming with sulphuric acid or leaching with strong hot sulphuric acid offer greater possibilities as methods of recovering zinc from residue.

If cheap power is available, smelting in an electric furnace offers attractive possibilities due to small gas volume and high recovery of metals. Residue is mixed with coal and lime rock and charged through the furnace roof. The slag bath acts as a resistor. The products are lead bullion, leady copper matte, and zinc-lead fume which is leached to recover zinc, the lead residue being returned to the furnace.

**Future of the Process.**—The present form of the process has been in use on a commercial scale less than 10 years, and, if the progress made during that period is any indication of future progress, another 10-year period will greatly extend its application and scope of usefulness. Already, many low-grade complex ores are being treated that would otherwise remain untouched, except during periods of very high metal prices, and it is reasonable to expect that the process will be further developed to care for additional ore supplies presenting only slightly different problems.

Roasting control to prevent the formation of ferrate offers a fertile field for further improvement. Much has been accomplished along this line since the early days of the process, but it is by no means certain that perfection has been attained. A different type of roasting furnace may be developed to aid along this line, the present type being adopted because of its standard design. Different methods of raking on the upper floors to vary the speed at which the feed is advanced across the floors, and more exact control of air supply and of hearth temperatures, are details that have not been sufficiently investigated to exhaust all possibilities of improvement with the present equipment.

Residue treatment or different leaching methods to recover more of the zinc now lost as ferrate, sulphide, and sulphate will be perfected and will materially reduce present loss. Improved purification methods to increase efficiency of zinc dust or development of a substitute for zinc dust will decrease zinc loss and operating costs.

Improvements in the purification of solution and the better regulation of cell operation will reduce power requirements, and, consequently, operating costs. Closer spacing of electrodes, higher average acidity, less loss of power through bar-line and electrode contacts, etc., will result in lower power consumption. Heavier zinc deposits from the cells and better furnace design and operation will reduce dross loss in melting

furnaces These and many other parts of the process will be improved from time to time until the process reaches a degree of perfection comparable to many of the older established metallurgical processes

None of the plants now operating is using the original flow sheet or process for which it was designed, equipment and buildings having been utilized to meet the changes made in the process A much more efficient plant than any of the present plants, from the standpoint of labor and material-handling costs, could now be designed As the present plants have maintained operations through periods of very low metal prices, it is safe to assume that another plant designed for more efficient operation, and with improved recovery of zinc, would be able to produce zinc in competition with any of the older pyrometallurgical plants

## CHAPTER XXXIII

### CHLORINE METALLURGICAL PROCESSES

BY STUART CROSDALE, PH. D.<sup>1</sup>

A brief history of chlorine metallurgical processes is a necessary introduction to the processes which are now in use. Processes which are no longer considered commercial on account of changed operating conditions were operated successfully by the present generation of metallurgists and are, therefore, entitled to historical records. Metallurgical problems are solved frequently by clues furnished from earlier experience.

#### EARLY HISTORY

Chlorine, as a metallurgical reagent for extracting metals from ores, has been used almost exclusively for the recovery of gold and silver. It has been used to some extent in the treatment of low-grade copper ores, but never in a major metallurgical process for the recovery of copper. The use of chlorine in the metallurgy of other base metals has been subsidiary.

High-grade gold and silver ores and high-grade base-metal ores containing small or large amounts of gold and silver are usually smelted to recover the metals. Chlorine has been associated only with hydrometallurgical processes (including amalgamation), usually for low-grade ores, but sometimes for high-grade siliceous ores remote from other facilities for treatment.

The earliest hydrometallurgical process for treating gold and silver ores was amalgamation. The date when mercury was first used for this purpose is unknown. Amalgamation of gold was known to the Romans and was recorded by Pliny, but no reference is made to silver. For the oxidized ores near the surface where the gold and silver were in metallic condition or the silver occurred as a haloid—this process was simple, but when deeper mining reached sulphide ores another method had to be devised to put these metals into a condition to be amalgamated.

The first recorded use of mercury in the metallurgy of silver, and in connection with it the first recorded use of chlorine in any metallurgical process, occurs in a treatise entitled "De la Pirotechnia," by Vanoecio Biringuccio, published in Venice in 1540.<sup>2</sup> In this treatise it is stated that the ore (previously roasted, if refractory) was finely ground in a stone mortar, screened wet, and dried. The dry ore was moistened with vinegar or water, in which had been dissolved mercuric chloride, copper sulphate, common salt, and sometimes ferrous sulphate. The ore pulp was then covered with mercury and ground, or stirred, in the mortar for an hour or two. The tailings were washed away with water and the silver was recovered by retorting the amalgam.

**The Patio process** for the treatment of silver ores, involving the same chemical reactions as those in the process just described, was invented by Bartolomé Medina, a miner of Pachuca, Mexico, in 1557.<sup>3</sup> The invention of this process

<sup>1</sup> Chemical and Metallurgical Engineer, Symes Bldg., Denver, Colo.

<sup>2</sup> Percy, John, 'Metallurgy of Silver and Gold,' pp 559-562, London, 1880.

<sup>3</sup> Percy, John, op cit., p 561.

is credited to Medina, in a report by Luis Berrio de Montalvo, addressed to the Viceroy of Mexico and printed in Mexico in 1643, and also in a memoir by Diaz de la Calle to Philip IV, printed in Madrid in 1646. Montalvo intimates that Medina derived his information from Spain that silver could be obtained from its ores by means of mercury and salt. The process was especially adapted to the arid regions of Mexico and South America, where fuel and water were scarce and transport expensive. It is still used to some extent in these countries and will be described in detail later.

The "Cazo" or caldron process was invented in 1590<sup>1</sup> by a priest, Alvaro Alonzo Barba, at Tarabuco, 24 miles from La Plata, Peru (now Bolivia). This process was the ancestor of the pan-amalgamation process. It was particularly adapted to the rich surface ores of that district containing chloride of silver, and it was also applied to silver sulphide ores to some extent. The process was conducted in a vessel made wholly of copper, or having a copper bottom. This vessel or caldron was provided with a vertical shaft, to which radial arms were attached for agitating the ore. Finely ground ore, water, and common salt were mixed together to the consistency of a thin pulp and placed in the caldron.

The caldrons, usually four in number, were placed on top of an adobe furnace built like a cook stove, and heated so as to keep the ore pulp at the boiling point. Mercury was added and the boiling pulp was stirred continuously for several hours, after which time the amalgamation was completed. The caldron was removed from the furnace, the tailings washed away with water, the amalgam recovered, and the process repeated with a new charge of ore. The active chemical reagents were the copper of the caldron and the boiling solution of common salt. The silver chloride in the ore was dissolved in the hot brine and reduced to the metallic state by the copper of the caldron, and then amalgamated by the mercury. The cuprous chloride formed was also dissolved by the salt solution and became active in converting the silver sulphide minerals into the chloride, although if a large amount of sulphide minerals were present preliminary roasting was recommended on account of the consequent loss of mercury. In later years iron was added to the caldrons to reduce and recover mercury that had become soluble or floured.

The Krohnke process, in which cuprous chloride was added to the hot salt solution to decompose the sulphide minerals, was introduced in Chile in 1860. The silver was recovered by means of zinc or lead used in the form of amalgam.

**Chloridizing Roasting.**—In Europe, where fuel, mechanical appliances, and better operating facilities were available, more complicated processes were developed to treat ores. Chloridizing roasting of silver ores was first introduced in Vienna by Born, and combined with the Cazo process in 1786 at Chemnitz in Hungary. The Cazo process was soon superseded in Europe by the barrel-amalgamation process, which was first installed on a large scale in 1790 at Halsbrucker Hütte, near Freiberg, Saxony. Metallurgical works had been established at this point since 1710, and chloridizing roasting with barrel amalgamation was used not only for the ores but also for metallurgical products, such as matte, blister copper, and speiss.

The chloridized ore or furnace product, still containing an excess of salt, was rotated in a wooden barrel with water and scrap iron until the silver was reduced to a metallic state. Mercury was then added to recover the silver as amalgam. Owing

<sup>1</sup> BARBA, ALVARO ALONZO, "El Arte de los Metales," 3d book, Spain, 1640, DOUGLAS and MATHEWSON, English translation, pp 149-194, New York and London, 1923

to the base metals present, which were also chloridized in roasting and reduced by the scrap iron, the bullion obtained was very low grade. Attempts to "destroy" the base metals by roasting at a higher temperature resulted in considerable loss of silver through volatilization with the base-metal chlorides, and the chloridizing roast was eventually used only on the low-grade ores containing the least amount of volatile base metals.

This led to the invention of the *Augustin process* and its introduction at the Gottesbelchung Hutte near Mansfeld, Germany in 1843. Later in the same year, the process was introduced at the Freiberg works. In this process ores were roasted

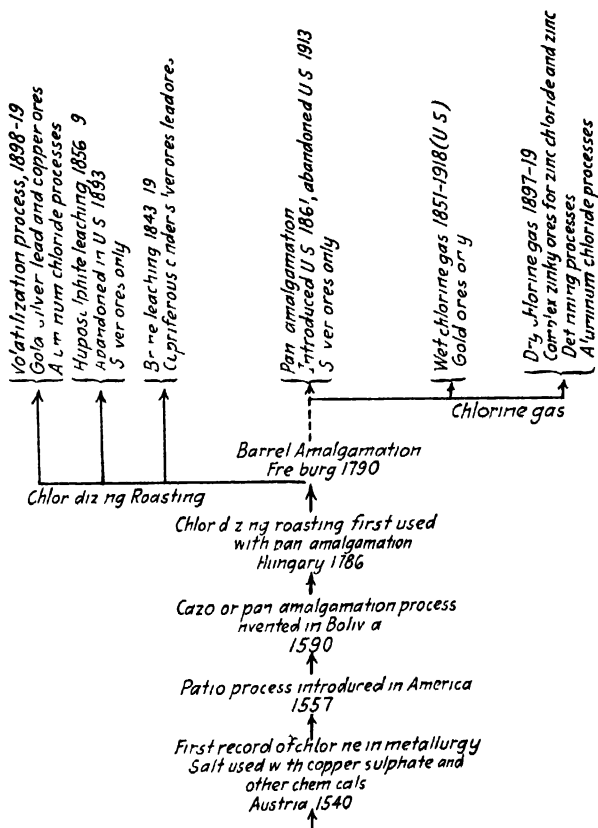


FIG. 1. The chlorine metallurgical tree.

with salt and then leached with a saturated solution of common salt. The silver chloride passed into solution, from which the silver was precipitated by metallic copper. The process was introduced at both Mansfeld and Freiberg to recover the silver from the copper mattes, but, owing to the imperfect extraction of the silver by the brine, it was soon abandoned and was superseded by the *Zurriogel process* in 1848, which was applied more particularly to mattes and furnace products than to the ores themselves. In this process no salt was used. The iron and copper were converted into oxides and the silver into sulphate by careful oxidizing roasting. The silver was then leached out by warm water and precipitated on copper.



**Hyposulphite Leaching—Patera Process.**—In 1848, Dr. John Percy, of London, suggested the use of sodium or calcium thiosulphate—incorrectly called hypsulphite—as a solvent for the chloride of silver after ores had been subjected to a chloridizing roast. The first practical application of this suggestion was made in 1856 by von Patera on the rich silver ores of the Joachimsthal district, Bohemia. To reduce losses by volatilization, von Patera introduced steam into the furnace during the chloridizing roasting. This process was first introduced in America by Ottokar Hofmann, in 1868, at La Dura, Sonora, Mexico, it was gradually adopted at other mines in Mexico and the United States, reaching the zenith of its application during the succeeding 25 years, until the demonetization of silver by the government of the United States in 1893 closed every leaching plant in this country that had been treating silver ore<sup>1</sup>

Up to this time, and for a number of years afterwards, gold in ores that had been subjected to a chloridizing roast was supposed to be converted into the chloride, which decomposed into chlorine and metallic gold at a temperature below 300°C. Hence, if gold occurred in silver ores, it was converted into metallic gold by chloridizing roasting and was not recovered by any of the solvents used for the extraction of silver.

**Plattner Process.**—Plattner proposed converting the gold into chloride by means of chlorine gas and extracting it with water. This process was introduced in Silesia, Germany, in 1851. The ore was either roasted “dead” or, if it contained silver, it was chloridized by roasting with salt. The silver was first leached out by brine or “hyposulphite” solution, then chlorine gas was applied to the ore in the vats. The gold was recovered by subsequent leaching with water and precipitating by means of ferrous sulphate (see “Wet Chlorine-gas Processes”).

**Longmaid-Henderson Process for Copper Ores.**—The treatment of copper ores by chloridizing roasting was first patented by Longmaid in 1844 and was first applied to the extraction of copper from pyritic residues or calcines by William Henderson of Scotland in 1859-1860.<sup>1</sup>

Pyrites from Spain and Norway, which were used throughout Europe for making sulphuric acid, contained from 3 to 8 per cent of copper. After the pyrites were roasted for the manufacture of sulphuric acid, the residues were again roasted with salt by the Henderson process, to convert the copper into chloride. The chloridized ore was then leached with water or dilute acid, and the copper was precipitated from the solution by iron.

The gases from chloridizing roasting contained sulphurous acid, hydrochloric acid, and chlorine. To prevent these gases from becoming noxious to the neighborhood, and to utilize their acids, they were passed through coke towers sprayed with water, which collected not only the acids but any volatilized metallic chlorides as well. The water from the scrubbing towers was used for leaching the chloridized ore.

This process was patented in the United States in 1866 and has been in constant use, both in this country and Europe, up to the present time. It will be further

<sup>1</sup> LISSLER, MANUEL. *The Hydrometallurgy of Copper being an account of processes adopted in the hydrometallurgical treatment of cupriferous ores including the manufacture of copper vitriol, with chapters on the sources of supply of copper and the roasting of copper ores*, pp. 87-104, London and New York, 1902.

described under the paragraph on copper ores in the section on Chloridising Roasting and Leaching Processes.

When the residues or ores contained silver, that metal was precipitated from solution as an iodide by the *Claudet process* before the precipitation of the copper.

**Hunt & Douglas Process.**—About the same time, 1862, ferrous chloride was suggested by Schaffner and Unger, of Germany, as a solvent for copper in ores. This method was developed later in the United States into the Hunt & Douglas process. It was designed to treat oxidized copper ores with siliceous gangue.

Ferrous chloride was made by dissolving copperas (ferrous sulphate) and common salt in water. An excess of salt was then added and the sulphate of soda was removed as much as possible by crystallization. This solution, therefore, became a brine solvent containing a soluble base-metal (ferrous) chloride. The process was applicable to raw ore containing oxide or carbonate of copper and was later applied to the separation of silver and copper in roasted matte, because silver minerals are likewise soluble in the brine as prepared. The copper was precipitated on scrap iron in the usual manner. If silver was present, it was first removed by precipitation on copper.

The Hunt & Douglas process passed through many modifications on account of the difficulty of treating ores containing any carbonate of lime or magnesia, both of which precipitate the iron from the solvent. It was abandoned many years ago and was replaced by smelting and electrolytic refining. Acid leaching has replaced it in hydrometallurgy.

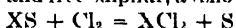
The *Doetsch process*<sup>1</sup> using ferric chloride as a solvent for copper, was invented about this same period to treat the sulphide ores at Rio Tinto. An attempt was made in 1914 to revive this process under the name of the *Slater process*,<sup>2</sup> but it did not pass the experimental stage. The feature of the Slater process was the regeneration of the ferric chloride. A lixiviant containing ferric chloride and hypochlorous acid was produced by suspending ferric hydroxide in the anode compartment of a cell in which a salt solution was electrolyzed. After the dissolution of the copper from the ore, ferric hydroxide was precipitated from the lixivium by means of the sodium hydroxide produced in the cathode compartment of the electrolytic cell. Under the highly oxidizing conditions in the solution, ferric hydroxide can be preferentially precipitated in this manner without precipitating any of the copper. The ferric hydroxide precipitate was returned to the circuit in the anode compartment for the generation of new lixiviant and the copper was recovered from solution by the usual methods. The only reagent required was common salt. The process was not adapted to basic ores. A slight modification of this process was developed by the Midland Ores & Patents Co.<sup>3</sup> at Waverly, N. J., in which the solution containing ferrous chloride, after precipitating the copper on iron, was regenerated direct by electrolysis, yielding ferric chloride for new lixiviant and metallic iron for copper precipitation (see p. 1171).

copper, by cooling to separate the lead chloride, by adding powdered limestone to precipitate the arsenic, antimony, and bismuth, and by the use of air in a special manner to precipitate the iron as oxide. It was then electrolyzed to precipitate part of the copper as pure metal, and to regenerate cupric chloride for leaching new ore. Owing to difficulties in manipulation, the process was not a commercial success.

**Hoepfner Process for Zinc Ores.**<sup>1</sup>—The ore was roasted with salt at a temperature not to exceed 650°C and leached with hot water. The solution was purified by cooling to 5°C to crystallize out the sodium sulphate, by adding bleaching powder and marble dust to precipitate the iron and manganese, and by adding powdered zinc to precipitate the other electronegative metals. The purified zinc and sodium chloride solution was electrolyzed for the production of metallic zinc and the recovery of chlorine to make bleaching powder. The process was used for a short time in Europe.

**Swinburne-Ashcroft Process for Complex Ores.**—The use of chlorine gas in the metallurgy of lead, zinc, and other base metals was brought into commercial prominence by Swinburne and Ashcroft of England, who obtained their first patents in 1897.<sup>2</sup> In the original process, as operated at Broken Hill, Australia, dry chlorine gas was applied under pressure to the dry and coarsely pulverized sulphide ore in a closed shaft furnace known as the "transformer." The chemical reactions involved are strongly exothermic and supplied all the heat necessary for operation. By regulating the flow of chlorine gas to the supply of fresh sulphide ore, a temperature of 600 to 700°C could easily be maintained in the transformer.

The reaction between dry chlorine gas and a mineral sulphide results in the formation of a metallic chloride and free sulphur, as shown by this equation:



At the temperature named, the sulphur distilled from the top of the transformer and the fused metallic chlorides, with the gangue in suspension, were tapped from the bottom. The metals were recovered by substitution, the fused chlorides, as they came from the transformer, were stirred into a bath of molten lead, which decomposed the precious metal chlorides and recovered these metals in the form of a high-grade lead bullion, from the lead bath the fused chlorides were drawn to another kettle and treated with zinc to recover the lead, the remaining chlorides were then dissolved in water and treated with chlorine gas to oxidize the iron and manganese, zinc oxide obtained by roasting high-grade blende, was added to this solution to precipitate the iron and manganese as oxides which were removed along with the gangue of the ore, by filtration. As will be seen by following this line of substitution, all of the original chlorine was ultimately combined with zinc and the filtrate from the iron and manganese oxides was a commercially pure solution of zinc chloride. In the final phase of this process the zinc-chloride solution was evaporated to dryness and the zinc chloride fused and electrolyzed for the recovery of metallic zinc and the regeneration of the chlorine gas.

The process was cyclic. There was no appreciable loss of chlorine at any stage of the operations and all of the substitution metals were produced by the process itself, but the process did not prove successful as designed and operated. Its operation was limited to sulphide ores or concentrates carrying not over 30 per cent gangue, in order to maintain the temperature required.

<sup>1</sup> GUENTHER, E., 'Electrolytic Zinc Extraction by the Hoepfner Process' *Eng Min J* (May 16, 1903), 750-752. *Mineral Industry* " 6, 668 and 675, 7, 743, and 9, 688.

<sup>2</sup> SWINBURNE, JAMES, 'Chlorine Smelting with Electrolysis,' *Trans Faraday Soc* (London), July 1, 1903, *Min Sci Press*, Aug 8 and 15, 1903. *Electrochem Ind* (now *Chem Met Eng*), 1 (Aug 1903), 412-413, 2 (Oct 1904), 404, 3 (Feb., 1905) 63-66, *Eng Min J*, Aug 1, 1903, STEINHART, O. J.,

'Chlorine Smelting,' *Min Sci Press*, Nov 28 1903. ASHCROFT, E. A. *Trans Inst Mining Met* (London) June 19 1901. "Mineral Industry" 9, 692-693, 10, 267 and 677-682.

A modification of this process was developed by *Baker and Burwell*, of Cleveland, Ohio, in 1904-1908<sup>1</sup>. The finely pulverized dry ore was placed in a porcelain-lined tube mill provided with lead-lined trunnions, and supplied with flint pebbles. Low-grade complex ores were treated, and in the absence of a high percentage of sulphur the temperature was kept down to 100°C. Dry chlorine gas was admitted to the tube mill and chemical action began at once. As the tube mill revolved, the pebbles ground off the metallic chlorides as fast as formed and constantly exposed fresh surfaces of ore to the action of the chlorine, they also broke up any lumps that might be formed. The free sulphur that was formed remained with the ore. If the temperature was allowed to get too high, considerable sulphur chloride was formed, which distilled off at about 150°C.

After chlorination was completed, the ore was discharged from the tube mill and leached with water, thus giving a clean solution of metallic chlorides free from sulphur and gangue. The metals were recovered from the aqueous solution by substitution. The gold and silver were precipitated on copper, the copper on lead, and the lead on zinc. After oxidation with chlorine gas, the iron and the manganese were precipitated by means of zinc oxide, and the zinc and the chlorine were recovered by the electrolysis of the fused chloride as in the Swinburne-Ashcroft process. A couple of experimental plants were erected in Montana in the years that followed but, owing to operating difficulties, they did not prove successful. The most serious difficulties were to evaporate zinc chloride solution without the formation of basic salts and the consequent loss of chlorine as hydrochloric acid and also the development of a satisfactory cell for the electrolysis of the fused zinc chloride.

About this time John L. Malm, of Denver, Colo., began experimenting with the Baker-Burwell process and has continued its modification and development up to the present time. This will be described as the *Malm process*<sup>2</sup> in the section on Dry Chlorine-gas Processes.

**Pohlé-Croasdale Volatilization Process.**—Loss of metals from volatilization during chloridizing roasting was known already when Plattner undertook a study of the conditions and extent of this loss in an elaborate series of experiments on both oxidizing and chloridizing roasting. The results of his experiments were published in his 'Metallurgische Rostprozesse' (1856). He mentioned considerable loss of silver chloride when it came in contact with other easily volatilized chlorides and discussed at length the volatile products of the chloridizing roasting, but he failed to record any loss of gold by volatilization.

Loss of gold by volatilization was recognized from time to time<sup>3</sup> and was the source of serious monetary loss in treating gold-silver ores by chloridizing roasting, but the cause of this loss seemed to be little understood. It was generally attributed to tellurium,<sup>4</sup> and not to chlorine, because the chlorides of gold were supposed to decompose into the constituent elements at a temperature below 300°C, therefore, all gold should remain in the ore in metallic condition. The first person to recognize chlorine

<sup>1</sup> BAKER CHARLES E. A New Application of Chlorine in Metallurgy. *Trans Am Electrochem Soc* (Oct 1907) 12, 155-163. *Electrochem Met Ind* (now *Chem Met Eng*) 5 (1907) 445. 6 (1908), 433. BAKER and BURWELL. Electrolytic Chlorination Process, *Min Sci Press* Feb 4 and 20 1905.

<sup>2</sup> TRAPHAGEN F. W. Dry Chlorination of Sulphide Ores. *Min Sci Press* (April 10 1909) 522. HERRICK R. J. The Malm Dry Chlorination Process. *Mines Minerals* (January 1910) 370. IONIDES, S. A. Dry Chlorination of Complex Ores. *Min Sci Press* (May 27 1916) 781. 787. MAIER C. G., Possibilities of Dry Chlorination of Oxidized Zinc Materials. *Eng Min J Press* 115, Jan 1923) 51-54.

<sup>3</sup> CHRISTY S. B. The Losses in Roasting Gold Ores and the Volatility of Gold. *Trans A I M E* 17 (1888-1889) 8. DEBRAY H. Note sur le chlorure d'or. *Compt rend* 69 (1869) 984.

<sup>4</sup> KÜSTEL GUIDO. Roasting of Gold and Silver Ores and the Extraction of Their Respective Metals without Quicksilver. p. 57. San Francisco 1880. CHRISTY S. B., *op cit* p. 3.

as the source of this trouble was C. H. Aaron,<sup>1</sup> but after many experiments on roasting California gold ores with salt he came to the conclusion "that gold is volatilized in some form not easily condensable."

Christy<sup>2</sup> investigated this subject in the best chlorination mills in California as well as in the laboratory during the early eighties, and came to the conclusion that losses of both gold and silver increase (1) with increased percentage of salt added during the roast; (2) with increase of time and temperature during roasting; and (3) when salt is added after a long oxidizing roast instead of at the start. Christy qualifies the last statement by saying that, "while there is a rapid volatilization of gold and silver when salt is added at the end of the roast, the gold chloride is quickly decomposed by the  $\text{SO}_2$  gases and by the raw ore itself in the cooler end of the furnace, and the gold is redeposited in metallic form, so that the actual loss is not so great as when salt is added at the beginning of the roast."

Stetefeldt<sup>3</sup> expressed his opinion that the gold escaped as a double salt, and, if this were true, the loss of gold depended on the volatility of the chloride with which the gold chloride was combined.

In an earlier treatise<sup>4</sup> Aaron states that the base metals are chloridized by chloridizing roasting, but they are not volatilized to any extent, while Kustel<sup>5</sup> takes the opposite view and states that "base metals as sulphates take up their share of salt and consume a large portion, but, as their chlorides are volatile, the salt is a means of getting rid of a great deal of the metals during roasting which are not desirable in the ore for subsequent treatment of silver."

The foregoing constitutes a brief summation of the knowledge of volatilization up to 1898. Much that is recorded is contradictory. There was no thought of making a commercial extraction by volatilization, and the recovery of the volatilized chlorides, if attempted, was only a phase of the general treatment of the ores.

In 1891-1893 Crousdale discovered that a commercially complete (above 90 per cent) volatilization of gold could be obtained from Cripple Creek ores by roasting with salt. About the same time, Pohlé independently obtained similar results with silver ores from Aspen, Colo. Systematic investigation of the volatilization of metals as chlorides was begun by these men in 1898 and was carried on with a large-scale experimental plant until 1903.<sup>6</sup> Numerous investigators<sup>7</sup> have worked on this process

<sup>1</sup> AARON, C. H., 'Leaching Gold and Silver Ores, the Plattner and Kiss Process, a Practical Treatise,' p. 121, San Francisco, 1881.

<sup>2</sup> CHRISTY, S. B. *op cit*, pp. 3-44.

<sup>3</sup> STETEFELDT, C. A., 'The Amalgamation of Gold Ores, and the Loss of Gold in Chloridizing Roasting, with Especial Reference to Roasting in a Stetefeldt Furnace,' *Trans. A. I. M. E.*, **14** (1886) 336-351.

<sup>4</sup> AARON, C. H., 'A Practical Treatise on Testing and Working Silver Ores,' San Francisco, 1876, pp. 35-36.

<sup>5</sup> KÜSTEL, GUIDO, *op cit*, p. 29.

<sup>6</sup> CROUSDAL, STUART, 'Volatilization of Metals as Chlorides,' *Eng. Min. J.* (Aug. 29, 1903), 312-314 (Sept. 19, 1903), 420. *Min. Mag.* London, (March 1914), 200-204. MATHER, HENRY A., *Eng. Min. J.* (Sept. 5, 1903 and Oct. 17, 1903), 576. HAWKINS, EDWIN N., *Eng. Min. J.* (Oct. 3, 1903), 490. ROSE, SIR T. K., 'Metallurgy of Gold,' p. 291, London, 1915.

<sup>7</sup> VARLEY, THOMAS and others, *Bull.* 211, U. S. Bureau of Mines, 1923, the chloride volatilization process of ore treatment, being a complete compilation of the work that has been done on this process. LAYNG, HAROLD R., 'Chloridizing Processes,' *Min. Sci. Press* (January 17, 1920) 77-83, 'Chloride Volatilization Process,' *op cit* (August 27, 1921) 284, 'Thermal Requirements of Chloridizing Volatilization,' *op cit* (Feb. 25, 1922), 264-266, 'Chloridizing Volatilization—Some Experiments and Their Practical Application,' *Eng. Min. J.* (Nov. 12, 1921) 764-770. BRADFORD, ROBERT H., 'The Volatilization Process at the Pope-Shannon Mine,' *Min. Sci. Press* (August 20, 1921), 263-266. VARLEY, THOMAS, and STEVENSON, C. C., 'Development of the Chloride Volatilization Process by the U. S. Bureau of Mines,' *Eng. Min. J.* (June 11, 1921), 991-993. VARLEY, THOMAS, 'Chloride Volatilization,' *Eng. Min. J.* (Feb. 18, 1922) 276-278. GAHL, RUDOLF, 'Heat Requirements in Chloridizing Volatilization,' *Eng. Min. J.* (June 3, 1922), 957-958. RALSTON, OLIVER C., 'Heat Requirements of Chloridizing Volatilization,' *Eng. Min. J.* (April 15, 1922), 614-615. HOWE, BEN, 'Gold Recovery by Volatilization,' *Monthly Journal*, West Australian Chamber of Mines (Dec., 1912), *Min. Mag.*, London (Mar., 1913), *Min. Sci. Press* (Mar. 29, 1913), 484, (Oct. 4, 1913), 585.

## CHLORINE METALLURGICAL PROCESSES

since that time. The process will be further discussed in the section on Chloride Volatilization Processes.

The sections which follow will treat of processes that are now in use, even though some of these processes have passed their metallurgical prominence; they will treat also of processes which are in the course of commercial development.

### CHLORIDIZING PROCESSES FOR RAW ORES

With the exception of the Malm process, these processes are necessarily confined to the treatment of surface ores, or to clean gold and silver sulphide ores in which the gold and silver sulphide minerals are not combined with base-metal sulphide minerals. To obtain a commercial recovery of the gold and silver, the base-metal sulphide minerals should not exceed 2 or 3 per cent; if more than this amount, concentration or roasting should precede the chloridizing process. Ores in which the silver is combined with arsenic and antimony as sulphides must be treated by chloridizing roasting to liberate the silver. Base ores containing carbonates of lime and magnesia are not adapted to these processes, owing to their precipitating action on the metallic chlorides, which prevents reaction on the silver minerals. The gradual disuse of these processes has been brought about by the world-wide depletion of surface or suitable ores and the necessity of other methods of treatment for the complex sulphide ores that come with deeper mining; also by the possibility of treating lower-grade ores on a larger scale at less cost by the cyanide process. Base-metal recoveries are made only with the Malm process.

The **Patio process** is still used in isolated districts of Mexico and South America, but with modern machinery and methods of transportation it has been almost completely replaced by the cyanide process and by the custom-smelting plant. A complete description of this process is given on page 1053. Therefore, a brief outline of its relationship to chlorine metallurgy will suffice here.

The salt and copper sulphate react to form sodium sulphate and cupric chloride. Some cuprous chloride is formed by the action of mercury on cupric chloride and this is dissolved by the brine in the ore pulp. Both cupric and cuprous chlorides react on the sulphides of silver, forming silver chloride and copper sulphide. The silver chloride is dissolved by the brine in the torta and the silver is precipitated in metallic form by the mercury, after which it is immediately amalgamated. Mercuric and mercurous chlorides are formed by the chemical reactions. Considerable silver sulphide is said to be reduced directly to metallic silver by the mercury, with the formation of mercuric sulphide.

The recovery of silver by this process will range from 75 to 80 per cent on favorable ores, but will drop below 60 per cent on ores containing an appreciable amount of base-metal sulphides, particularly blende or arsenical and antimonial sulphide minerals.

There is a chemical loss of mercury in the form of soluble chlorides, as well as a mechanical loss due to the flouring of the mercury by surface chemical action of sulphide minerals, but the total loss is not so much as would be expected. It is said to amount to about one and one-half times the silver recovered.

This process is applicable only where labor and the few necessary supplies are cheap, equipment and freight are costly, and time of little importance. For example, the Noche Buena and Feliz Ano mines in the Totolapam district, about 75 miles east of Oaxaca City, Mex., still have in active operation six patios and are preparing to

build six more. Extraction by the patio process is reported by the manager to be unusually high. Excessive freight rates, by mule back transportation, on stamp mill concentrates—65 pesos per ton—have caused the mine owners to enlarge their patio facilities<sup>1</sup>

The Pan-amalgamation process was evolved from the "cazo" or caldron process. In Europe, where it was first used, the amalgamating was done in revolving barrels and was known as the "barrel amalgamation" process. Pan amalgamation seems to have been an American development and it was first operated in the United States at Washoe, Nev., in 1861. For a long time it was known as the "Washoe process."

The "pan" was made wholly of cast iron, or with a cast-iron bottom and wooden sides. In either case the bottom was made hollow for the introduction of steam to heat the charge. Cast-iron mullers for grinding, stirring, and amalgamating the ore were attached to a vertical shaft in the center of each pan. The capacity of each pan ranged from 0.5 to 2 tons of ore and was usually about  $1\frac{1}{2}$  tons.

The ore was first crushed by jaw crushers and then by stamps or ball mills. If crushed wet, the excess of water was removed by settling tanks. The crushed ore from the settling tanks was then shoveled into the pans. Salt and copper sulphate were added in the ratio of 5 to 10 lb. of salt and  $2\frac{1}{2}$  to 5 lb. of copper sulphate per ton of ore. When the ore is free from interfering minerals, the salt has been reduced as low as 2 lb. and the copper sulphate to  $1\frac{1}{4}$  lb. per ton. Water was added in sufficient quantity to make a thin mud and steam was admitted, not only in the jacketed bottom of the pan, but sometimes into the ore itself, until the charge in the pan was maintained at the boiling point. The grinding and stirring of the charge was continued for 2 or 3 hr., in which time the chemical action was completed.

Mercury, equal to 10 per cent of the weight of the ore, was then sprinkled over the ore pulp by straining through canvas or chamois and the stirring continued for 3 hr. longer—when amalgamation was completed.

The whole charge was then washed from the pan into a settling tank provided with radial arms, and agitated under a constant flow of water until the amalgam collected in the bottom of the tank and the tailings were washed away. The amalgam was then transferred to a small pan known as the clean-up pan, where it was stirred with additional mercury and washed with water until free from ore particles. The silver and gold were finally recovered by retorting the amalgam.

The chemistry of this process is the same as that of the Patio process, except that the iron of the pan and mullers also acts as a reducing agent, not only for precipitating silver in metallic state from its chlorides but also for preventing the formation of any chlorides or sulphides of mercury, and in this manner avoids the chemical loss of mercury mentioned under the Patio process. The ore must be siliceous or neutral in character to avoid precipitation and the loss of effective copper salts by the carbonates of lime and magnesia.

Two important modifications of the process were developed later. The first was known as the Boss process, in which the ore from the stamp mill was finely ground in pans and then flowed continuously through a series of amalgamating pans and settling tanks. This made the process continuous and saved considerable time and labor in transferring the charges from settling tanks to pans and from pans to settling tanks. The other modification, where economic conditions were favorable, was the introduction of the chloridizing roast previous to pan amalgamation. By this means the silver sulphide minerals, as well as the base-metal sulphides, were converted more completely into the chlorides in the roasting furnace, and the addition

<sup>1</sup> *Eng. Min. Jn.-Press* (Sept. 5, 1925), 386

of salt and copper sulphate to the pan was rendered unnecessary unless the ore was insufficiently chloridized during roasting

The pan-amalgamation process was well adapted to surface or oxidized silver-gold ore where the gold was subsidiary in value and not amenable to ordinary amalgamation and where the silver occurred as a haloid, or, if it occurred as a sulphide mineral, the ore was comparatively free from the base-metal sulphides. With such ore the recovery averaged between 80 and 85 per cent, the process was metallurgically clean; it yielded a product of bullion and involved no troublesome by-products; it was simple to operate, the supplies needed were cheap and easily obtained

The disadvantage of the process was the small capacity and consequent high operating cost per unit of equipment, namely, one pan. This has been the principal reason for the abandonment of this process and its replacement by leaching processes, particularly the cyanide process. The last two notable and eminently successful examples of the pan-amalgamation process in the United States were at the Commonwealth mine, Pearce, Ariz., and at the Presidio mine, Shafter, Tex.

At the Commonwealth mine the ore was almost pure quartz, the ore milled averaged 15 oz. silver per ton, the silver occurred principally as a haloid. The gold was subsidiary in value and averaged 0.05 oz. per ton. The first mill, built in 1896, had a capacity of 200 tons daily, which was large for pan amalgamation. The ore was crushed dry in Jenisch ball mills, but these were not entirely satisfactory, and after a fire in 1900 they were replaced by stamps and the ore was crushed wet. The mill operated until 1910, when the cyanide process was introduced. The recovery by pan-amalgamation was 77 per cent on 15-oz. ore, the average cost of milling was \$1.60 per ton for the 400,000 tons treated, the loss of mercury was 0.2 lb. per ton of ore.

At the Presidio mine<sup>1</sup> the ore was a siliceous limestone averaging 18 oz. of silver per ton, principally as a chloride. The ore also contained some galena. A pan-amalgamation mill of 70 tons daily capacity was built in 1884 and operated continuously until 1913, when it was converted into a cyanide plant of larger capacity. The average recovery by pan-amalgamation is reported to have been 85 per cent. So far as the writer knows, the reconstruction of this mill marks the extinction of the pan-amalgamation process in the United States, but the process is probably still used to some extent in South America. It is not without merit and can be safely recommended under favorable conditions.

**The Malm process** is especially adapted for the treatment of complex base-metal ores in the raw state. This process will be described in the section on Dry Chlorine-gas Processes.

## CHLORIDIZING ROASTING AND LEACHING PROCESSES

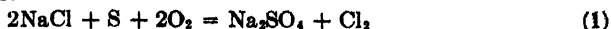
**Chloridizing Roasting.**—The gradual exhaustion of oxidized ore and the increase of base-metal sulphide minerals with the silver sulphide minerals, together with the increased facilities for transporting fuel and supplies, led to the introduction of chloridizing roasting and the attendant leaching processes.

In chloridizing roasting, furnace heat replaces water in effecting the desired chemical reactions, namely, that of breaking up the sulphides in the natural minerals and converting the metals into their respective chlorides. This is done by roasting the ore with common salt and a proportionate amount of sulphur in almost any type of roasting furnace. If too much sulphur is present in the ore, the excess is removed by preliminary roasting, if the ore is completely oxidized, sulphur is usually added in the form of pyrite or native sulphur in sufficient quantity to complete the reaction.

<sup>1</sup> ADKINSON, HENRY M., "The Silver Mine of Texas," *Eng. Min. J.* (Aug. 2, 1902), 150-151.

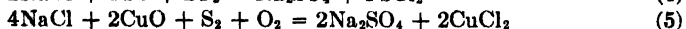
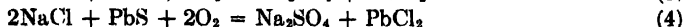
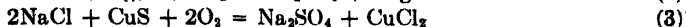
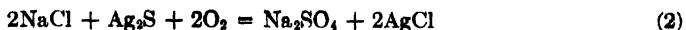


The reaction between the salt and sulphur, when heated in the presence of air, is shown by the following equation:



From this equation it is obvious that an excess of sulphur in an ore is an unnecessary consumer of salt.

For the metals that are converted into chlorides by chloridizing roasting, the following equations will indicate, in their simplest forms, the chemical reactions that occur in the furnace:



The equations for oxidized ore apply also to the carbonates, which decompose to the oxides on heating. Sulphates and silicates decompose salt by the direct interchange of the elements and radicals without the addition of sulphur.

Iron pyrite loses one atom of sulphur at low temperature, which assists in decomposing salt for the chloridization of oxidized ore, as indicated above. The ferrous sulphide formed by the loss of this atom of sulphur reacts with salt in the presence of air to form ferrous chloride in a manner similar to the other metals. This salt is probably oxidized to the ferric chloride *in transitu* to the oxide of iron, but in either state it decomposes at low temperature and becomes an active chloridizing agent for the other metals. Comparatively little chloride of iron is ever found in leaching solutions or in fumes from chloridizing roasting. The iron oxide thus freshly formed undoubtedly becomes an active catalytic agent and assists in the above-mentioned chemical reactions.

There are good reasons for believing that basic chlorides and double chlorides are also formed, but these need not be speculated upon here. Arsenic and antimony, which are frequently found in silver minerals, probably form combinations of this character. The method of calculation stated above has been found to be remarkably dependable in practice, but it must be remembered that, in roasting, there is a dry mixture of ore and salt, both of which are crushed to pass, on the average, a 0.75-mm. screen. It is, therefore, impossible to get the intimate contact between the salt and the mineral particles that is obtained from a solution of salt and finer grinding of the ore. For this reason, and on account of volatilization and mechanical losses, it has been found advisable, while maintaining the ratio between the salt and sulphur, to increase the proportions of both about 25 per cent in relation to the ore; also, for the reasons above mentioned, it is needless to say that these computations cannot be applied to a silver ore containing no chloridizable base metal, because the amount of salt necessary to combine with silver alone would be almost negligible and it would be difficult to bring about chemical reactions.

From Eq. (1) it will be observed that 116 parts by weight of salt combine with 32 parts by weight of sulphur, or, in practice, it may be said that the ratio of salt and sulphur is as 4 : 1. If sulphur occurs in the ore, this ratio will govern the amount of salt required for an efficient chloridization. The amount of sulphur that will yield the best results is that which will combine with chloridizable metals to form their normal sulphides. For example, as shown in Eq. (3), 65 parts by weight of copper combine with 32 parts by weight of sulphur to form normal copper sulphide, or a ratio of copper to sulphur as 2 : 1. Therefore, an ore containing 4 per cent copper would require 2 per cent sulphur and 8 per cent salt to yield the most efficient chloridization. By the same method of computation, a 7 per cent lead ore would require less than 1 per cent sulphur and 4 per cent salt for chloridizing roasting.

In the early days of chloridizing roasting there was a tendency to use higher percentages of salt than necessary. Later practice reduced this amount and it now ranges from 5 to 15 per cent of the weight of the ore, depending somewhat on the amount of sulphur present. Ten per cent is usually the maximum required for all ore treated by this process, and for this amount of salt the sulphur should be as near as possible to 2.5 or 3 per cent.

In the chloridizing roasting of silver ores, the roasting furnace does little more than start chemical action. For example, the ore-salt mixture remains in a Stetefeldt furnace only a few seconds while dropping from the top to the bottom—a distance of about 40 ft.—against an up draft. The red-hot ore is drawn from the furnace and dumped into a “soaking-pit,” or bedded on a cooling-floor to a depth of 3 or 4 ft., where it remains several days until cool. More than 50 per cent of the chloridization is done on the cooling-floor.

The temperature of chloridizing roasting should not exceed 600°C., which is a low red heat. Above this temperature there is considerable loss of the metallic chlorides by volatilization. Gangue materials and water vapor, as a rule, have little influence on chloridizing roasting at low temperatures. Gargue<sup>1</sup> states that aluminum silicates begin to decompose salt at 550°C. Spring<sup>2</sup> states that lead chloride begins to decompose in the presence of water vapor at 110°C. and even sodium and potassium chlorides are partially decomposed at 400°C. Bagdasarian<sup>3</sup> found that water vapor, diluted with air, decomposes zinc chloride at temperatures as low as 500°C. This phase of chloridizing roasting will be discussed under Chloride Volatilization Processes.

Practically all types of roasting furnaces have been used for chloridizing, namely, hand reverberatory, Bruckner, White-Howell, Stetefeldt, McDougall, Edwards-Merton, Wedge, Herreshoff, and Holt-Dern. Descriptions of these furnaces can be found in any standard treatise on metallurgy and those that have gone out of use will not be mentioned further here.

The most satisfactory type of furnace yet developed for ordinary chloridizing roasting, and the one most universally used at the present time, is the Wedge or “multiple-hearth” furnace, in which the ore and salt mixture is fed at the top and raked from one hearth to the next by rabbles or plows attached to radial arms from a vertical central shaft. This furnace is usually made with five superimposed hearths 20 ft. in diameter. It is fired at the bottom hearth with wood, coal, oil or gas from an attached fire box. The coal required is about 10 per cent of the ore charge, depending upon the quality of the coal used and the amount of sulphur in the ore. The capacity of such a furnace is 80 tons of charge (ore and salt) per day, although with careful manipulation it has reached 100 tons per day.

The Edwards-Merton is less complicated in construction than the Wedge furnace. It requires no specially designed fire brick or tile. The mechanical parts are simple in construction and easily obtained. These are requisites in isolated districts (see Brine Leaching of Silver Ores).

The Holt-Dern furnace, a recently developed type, has been applied to chloridizing silver ore at Tintic, Utah. It is a low, shaft furnace, built of concrete, and provided with a rocking, self-dumping grate for discharging the roasted ore. The furnace is filled with a moist mixture of pulverized ore, coal, and salt. A low air blast is applied to facilitate combustion. New ore mixture is charged at the top, while the chloridized ore is drawn intermittently from the bottom. The operation of the furnace will be further described under Brine Leaching of Silver Ores.

The Stetefeldt furnace went out of use with the passing of hyposulphite leaching in the United States but recently it has been revived in modified form for oxi-

<sup>1</sup> GARGUE, A. *Compt rend* 102 (1886), 1164, *Ann Chim Phys* (6), 10 (1887), 105, BAGDASARIAN, A. B. “Influence of Certain Solids and Gases on the Chloridization Roast,” *Eng. Min. Jn. Press* (June 13, 1925), 963.

<sup>2</sup> SPRING, W., *Berichte* 18 (1885), 344-345; BAGDASARIAN, A. B., *op. cit.*, 963.

<sup>3</sup> BAGDASARIAN, A. B., *op. cit.*, 964.

dising roasting of flotation concentrates; it also has merit as a chloridizing furnace, for which it was originally designed.<sup>1</sup>

Where higher temperatures are used, as in volatilization roasting, the modern development of the White-Howell furnace is the only type that has been found satisfactory. This is the regular cement kiln used for burning clinker. It is a cylinder 100 to 125 ft. long and lined with fire brick. It is fired directly with oil, producer gas, or powdered coal, at the discharge end.

Dust losses are negligible in chloridizing roasting, because as soon as the temperature is high enough to start the sulphur burning, which is below a red heat, chemical action begins and the roasting charge has the appearance and physical character of having been wet with water. Losses that may occur are due to the volatilization of metallic chlorides as fume at high temperatures, and not to mechanical loss as dust.

Following chloridizing roasting there are, necessarily, attendant processes for the recovery of the metals. These are described chronologically in the following paragraphs.

**Pan Amalgamation.**—For a long time the pan-amalgamation process was used to recover silver and gold from ore that had been chloridized by roasting. The process was the same as that used on raw ores, except that the addition of salt and copper sulphate to the ore in the pan was unnecessary unless the chloridizing roasting was poorly done. This process was gradually superseded by leaching processes, for reasons already stated.

**Brine Leaching of Silver Ores.**—The actual leaching of silver ore with brine, after chloridizing roasting, began with the Augustin process in Germany in 1843 and continued to be used in Hungary for the recovery of silver from matte up to 1893. Owing to the prevalent use of pan amalgamation—even for ore which had been chloridized by roasting—and the early introduction of hyposulphite leaching, brine leaching of silver ore did not make much progress in the United States. It was first successfully applied by D. W. Brunton at the Stewart mill in Georgetown, Colo., in 1876. Later, he operated this process at the Caribou mine in Boulder County, Colo., and, up to 1879, at the Silver Peak mine in Nevada. Brückner furnaces were used for chloridizing roasting. No effort was made to recover any base metal except the copper used in precipitating the silver from solution. The process was not revived for the commercial treatment of silver ore until 1911, when the Holt-Dern process<sup>2</sup> was developed at Park City, Utah, and reached commercial operation in 1914. In 1915 a plant was constructed at Silver City, Utah, by the Tintic Milling Co. This plant is now dismantled, but, during its operation it became essentially a pilot mill for a larger plant constructed by the Standard Reduction Co. at Harold, Utah, to treat the low-

<sup>1</sup> **Vanadium Ores**—The United States Vanadium Co. operates a plant at Rifle, Colo., for the treatment of siliceous vanadium ores (roscoelite?) found in the sandstone beds of that vicinity. The ore carries about 35 per cent vanadium oxide. It is roasted with salt at low temperature and sodium vanadate is formed instead of vanadium chloride. The roasted ore is leached with water and the  $V_2O_5$  is precipitated from the solution by the addition of sulphuric acid. This high-grade precipitate is filtered off, washed, dried and shipped to the ferro-alloy plants in eastern United States.

<sup>2</sup> **HOLT, THEODORE P.**, "Chloridizing Leaching at Park City," *Trans. A. I. M. E.*, 49 (1914), 183-197; **SCHMIDT, F. S.**, "Rejuvenating the Chloridizing Roast," *Min. Sci. Press* (Aug. 29, 1914), 324-328; **SCHMIDT, GEORGE H.**, "Park City Milling Co.," *Eng. Min. J.* (Aug. 8, 1914), 254; **DERN, G. H.**, "The Mines Operating Co., Park City, Utah," *Eng. Min. J.* (Aug. 8, 1914), 253; **KEEF, GLENN A.**, "Chloridizing Blast Roasting and Leaching," *Eng. Min. J.* (Feb. 6, 1915), 265-269, and (Feb. 13, 1915), 315-322; **HOLT, THEODORE P.**, "Chloride Roasting and Leaching, Tintic Milling Co.," *Min. Sci. Press* (Apr. 24, 1920), 603-604.

grade silver-lead ore from the Tintic Standard mine. The operations of the pilot plant were largely experimental and further reference to them is unnecessary. The larger plant has a capacity of 200 tons per day and has been operated continuously since it started in January, 1921.

The process<sup>1</sup> consists of a chloridizing roast in a Holt-Dern furnace, followed by a percolating leach with a nearly saturated solution of common salt acidified with sulphuric acid. The silver is recovered by precipitation on cement copper, and the copper and lead by precipitation on detinned scrap iron.

The recovery of lead at the start was to be incidental, as it was at the pilot plant, but, stimulated by the higher prices for the metal during the last few years, effort has been made to improve the recovery—which was less than 50 per cent—and to treat ores containing a higher percentage of lead than was accepted formerly.

The average analysis of the ore treated during 1924 was as follows. Au, 0.025 oz per ton, Ag, 18.26 oz per ton, Cu, 0.3, Pb, 5.0, SiO<sub>2</sub>, 65.0, Fe, 10.0, CaO, 0.7; S, 3.0; and As, 0.7 per cent. It is essential that the lime content of the ore be low, the sulphur not exceed 4 per cent, and the gold be negligible.

The ore mixture is made up as follows. The ore, with 8 to 10 per cent salt, is crushed to pass a 10-mesh screen (about 1.8 mm opening). Fuel is added in the form of coal dust, usually between 1 and 2 per cent, depending on the amount of sulphur (as sulphide) in the ore. With 3 per cent sulphur, 1.5 per cent coal is used, as the sulphur changes the coal is varied, using the ratio of sulphur coal = 1.065. Sulphur is maintained as near 3 per cent as possible, if the sulphur content falls below 2 per cent, the charge burns unevenly and loses heat rapidly during the recharging period, if it exceeds 4 per cent, the charge fuses in the furnace, becomes troublesome to handle, and is poorly chloridized. Water is a necessary constituent of the charge for the purpose of agglomeration and forming a more porous ore-bed. It is added in sufficient quantity to make the ore stick together when pressed in the hand. With a 10-mesh feed the water required amounts to about 7 per cent, too much water makes a hard calcine, too little makes roasting slow with a tendency to be 'spotty'. Water is supposed to assist in the chloridization by the formation of hydrochloric acid.

The feature of this process is the unusual type of chloridizing furnace which has been described at the beginning of this section. The Holt-Dern roasters consist of a row of reinforced-concrete boxes, 7 by 9 ft by 5 ft deep inside, set end to end, on the bottom are mechanically operated grates with hoppers underneath. Leading into the hoppers under the grates, is a pipe through which an air blast is supplied at 8 oz pressure by a direct-connected Sturtevant fan. This arrangement helps to cool the roasted ore and heats the air blast. A common flue, through which the gases are drawn, runs the full length of the furnaces and connects with the absorption chamber for the recovery of acid, and thence to the stack.

The furnace is started with a layer of coal dust dampened with oil, spread over the grate, and ignited. This is followed with a special ore mixture, richer with coal than the charge. The air blast is turned on, and when this charge is burning properly the regular charge is added. At regular intervals the grate mechanism is set in motion and the charge is lowered in the furnace, so as to leave a bed of red-hot calcines, about 10 in. deep, on the grate to start the new charge burning. As the roasted ore is drawn from the furnace, new ore mixture is added at the top in 4.25-ton charges. The capacity of each furnace is about 25 tons of calcines per day. The temperature in the center of the roasting ore is supposed to be between 700 and 750°C. The furnace is operated with a cold top to prevent, as much as possible, loss by volatilization.

<sup>1</sup> ALLEN, H. P. and MADGE, W. C., 'Chloridizing Mill of the Standard Reduction Co.' *Trans. A. I. M. E.*, (Sept., 1925) *Min. Met.*, (Aug., 1925), 444. PARSONS, A. B., 'The Tintic Standard Reduction Plant,' *Eng. Min. J.-Press* (Aug. 22, 1925), 284. OLDRIGHT, G. L., 'Present Trend in Treatment of Complex Ores,' *Min. Met.* (July, 1924), 346.

The hot chloridized ore is dropped from the hoppers into a concrete launder through which a stream of brine or "weak" mill solution is flowing. This flushes the calcines into one of six concrete leaching vats. These vats are 28 ft. in diameter by 11 ft. deep inside, and have a filter bottom made up of crushed quartzite. Each vat will hold about 225 tons of calcines when filled within 8 or 10 in. of the top. After leveling the charge, leaching is started. The lixivium is drawn through 3-in. earthenware cocks into two concrete tanks of the same size as the leaching vats. The first, or richer part of this lixivium, is designated as "pregnant solution" and carries about 3 oz. silver and 14 lb. lead per ton; the subsequent lixivium, known as "weak solution," is discharged into the second tank and is used for sluicing calcines into the leaching vats.

The hot lixiviant obtained in the manner above described, containing an excess of salt and the soluble base-metal chlorides derived from the chloridizing roast, forms a quick solvent for the silver chloride and some of the lead salts in the ore. It is necessary to maintain a slight acidity (varying from 2 to 5 lb. of acid to the ton) in the leaching solutions at all times. A small part of the supply is derived from the gas-scrubbing chamber through which the gases from the roasting furnaces pass, but it is necessary to maintain the greater part of this acidity by the direct addition of 66°B. sulphuric acid. The water from the scrubbing chamber probably contains a mixture of sulphuric, sulphurous, and hydrochloric acids. The regular lixivium from the leaching vats contains about 22 per cent salt and has an average temperature of 62°C.

The time cycle for leaching the chloridized ore is distributed as follows: filling the vats, 24 hr.; leaching with weak solution, 48 hr.; with barren solution, 48 hr.; with wash water, 8 hr.; draining, 2 hr.; emptying vats, 8 hr.

The presence of lime and magnesia is objectionable in an ore because they combine with the sulphur and prevent chloridization in the roasting furnace; they consume acid in the leaching solutions; and they have a precipitating action on the base-metal chlorides. Gold in the ore is only slightly chloridized and the recovery never exceeds 35 per cent. Gold, therefore, is not desired and if it occurs in the ore in appreciable quantity it must be recovered from the tailings by another process. Chlorine gas added to the leaching solutions will give a good extraction of the gold, but it has not been found feasible to use this in practice. The recovery of gold will be further discussed under Chloride Volatilization Processes and Wet Chlorine-gas Processes.

A lixiviant saturated with salt has been found troublesome to handle in commercial practice, and it apparently does not have the solvent power for silver chloride that is obtained by slightly weaker solutions. The mill solution, as now constituted at the Standard plant, has a carrying capacity of 25 to 30 oz. silver per ton, which is a concentration not approached in practice. Dissolution of the lead, however, is quite a different problem. Lead in the calcines is considered as present in the form of the sulphate and not as the chloride. The quantity of lead salts that brine will carry depends on the solution temperature, the chlorine concentration, and the sulphate content. An equilibrium in the sulphate content is soon established in mill solutions, which prevents further dissolution of lead salts. If the sulphate content (expressed as  $\text{Na}_2\text{SO}_4$ ) could be kept below 2 per cent in the mill solutions of the Standard plant, it would be possible to recover about 1.25 tons additional lead per day; but, as these solutions are returned to the circuit, the sulphate content is constantly increased by the addition of acid, and by the sulphates from new calcines. All known methods for removing these sulphates are prohibitive on account of the expense. Increasing the leaching time from 4 days to 9 days, raised the recovery of the lead from 65.7 per cent to 92.5 per cent, but this procedure would require greatly increased leaching capacity.

Formerly, the silver was recovered from solution by precipitating on copper plates. The precipitate was melted into bullion 975 fine. Now, the silver (and gold) are precipitated by cement copper (produced by the process) passed countercurrently to the lixivium through four Pachuca agitators. These tanks are made of concrete and the agitation is done with compressed air. After a certain period the copper the first agitator ceases to function, this has been attributed to the deposition of metallic arsenic. The silver precipitate is then withdrawn from the first agitator and the copper from the second agitator is by-passed into the first. The average analysis of the silver precipitate is, Ag, 8750 oz per ton (30 per cent), Cu, 15; Pb, 2; As, 25; Sb, 15 per cent, and the remainder is principally iron, alumina, and "insoluble." This precipitate is washed and roasted slowly in a small reverberatory furnace. The arsenic is volatilized and recovered in bags as  $As_2O_3$ , the temperature is then raised to oxidize the copper. The roasted material is treated with hot, dilute sulphuric acid (25 per cent), which dissolves the copper. The residue is dried and sold to the smelting companies. The analysis of the final silver product is, Ag, 10,000 to 14,000 oz per ton, Cu, 10, As, 0.75, and Pb, 1.4 per cent.

The lixivium leaving the Pachuca agitators flows through eight precipitating boxes or launders for the recovery of the copper. These boxes are 30 ft long, 5 ft wide and increase from 18 in. to 3 ft in depth, they are made of concrete in the usual form; the bottoms slope to facilitate sluicing. Ordinary scrap iron was formerly used as a precipitant, but now detinned sheet scrap is used in order to supply greater precipitating surface and to produce a higher grade copper precipitate. At comparatively low temperatures, the copper is precipitated preferentially from the lead. Part of the cement copper thus produced, is used to precipitate the silver and the balance is shipped to the smelters, it contains about 100 oz Ag per ton, 50 per cent Cu, and 6 per cent Pb, besides iron and other impurities.

The lead also is precipitated on detinned scrap sheet iron, but, to get a sufficiently rapid action, the temperature of the solution must be maintained above 75°C. The solution leaving the copper precipitating boxes has a temperature of about 45°C; this is pumped into a tank fitted with copper coils and is heated with low-pressure steam to the required temperature before going to the lead precipitating boxes. The lead precipitating boxes are fifteen in number and are of the same size and form as the copper precipitating boxes. The lead precipitate contains 65 oz Ag per ton, 70 per cent Pb, and 5 per cent Cu, besides iron, alumina, and other impurities, it is shipped to the smelters without drying and contains 21 per cent moisture. The iron and the alumina in the copper and the lead products are probably in the form of basic salts.

It has been found advantageous to remove the tin from the tin-plate scrap before using the iron as a precipitant. This is accomplished by treating the scrap with a solution of caustic soda containing a small amount of litharge.<sup>1</sup> The litharge is obtained by roasting the lead precipitate. The tin is not recovered.

The average recovery of the metals from the ore is, gold, none, silver, 89.8 per cent; lead, 65.7 per cent, copper, 52.2 per cent.

The cost of mill treatment per ton of dry, crude ore is, operating labor, \$1.738; operating supplies, \$1.319, repair labor, \$0.553, repair supplies, \$0.539, power, \$0.283 total, \$4.432. The cost of labor and supplies at the plant is, labor, \$5 per 8 hr day; salt, \$4; slack coal, \$3.05, and tin-plate scrap, \$18 per ton.

The concrete construction used in the leaching vats, precipitating boxes, and tanks, is important. The aggregate was composed of crushed quartzite and siliceous sand containing 96 per cent  $SiO_2$ . The maximum size of the aggregate was 1.5 in.; the proportions used were 65 per cent of the coarse and 35 per cent of the fine. The ratio of cement to aggregate varied from 1:3 to 1:4, except in the lead and copper precipitating boxes where a ratio of 1:5 was used. None of this concrete has shown

<sup>1</sup> SCHNABEL CARL, "Handbook of Metallurgy," 2, 423 New York and London, 1898.

any deterioration from the corrosive solutions except the walls of the absorption chamber, where the gases from the roasting furnaces are sprayed; these walls have been attacked by the acids and are now protected by plank, painted with elaterite. Cracks occasionally develop in the lead precipitating boxes, due to the change in temperature when washed with cold water, such cracks are chipped out and filled with a 1:1 cement mortar.

The mill is placed on a steep hill-side and the solutions are moved by gravity as much as possible, where pumping is necessary, wooden air-lift pumps are used for the corrosive solutions, and acid-proof centrifugal pumps handle the barren solution. The launders are made of concrete.

Considerable space is devoted here to the description of this plant because it represents years of experimentation and the expenditure of a large amount of money in an effort to exploit a new principle of ore roasting on an old metallurgical process, brine leaching of silver-lead ore has been studied here also in great detail under modern and most favorable conditions. The results as a whole show that little, if any, pecuniary advantage has been gained over shipping the ore to the local smelters; this fact does not reflect adversely on the merit of the brine leaching process, but clearly illustrates how local conditions, not only should govern the selection of an ore treatment process, but may affect its commercial value.

The interesting and novel features of the plant have been the roasting furnaces and the use of concrete construction. The basis of success in chloridizing roasting and leaching processes is an efficient chloridization, consequently, the interest in this plant centers primarily in the furnaces used for chloridizing roasting.

Whatever economies may be obtained in the construction and operation of the Holt-Dern furnace, it is fundamentally wrong for chloridizing roasting. Highly oxidizing conditions are imperative for efficient chloridization, these conditions cannot be obtained when carbonaceous material is mixed with the ore charge and used as fuel. The reducing conditions in this furnace are amply proved by the tendency of the ore to matte or fuse when the sulphur content exceeds 4 per cent. At the low temperature maintained, the effective chlorine can be liberated from the salt only by the sulphuric acid radical, the sulphuric acid radical can be formed only by supplying the elemental sulphur with sufficient oxygen. Apparently, to obtain these essential oxidizing conditions, it would be better to use a percentage of sulphur high enough to maintain the heat of chemical reaction and use no coal at all. It is necessary also, in the operation of these furnaces, to use an ore charge too coarse for efficient chloridization, in order to maintain sufficient draft, unless the mineral particles are freed from the gangue by the coarse crushing, it is impossible to chloridize a mineral particle entirely enveloped by gangue. The ore mixture should be crushed to pass a 20 or 30-mesh screen for proper chloridizing roasting.

Water cannot possibly have any chemical influence on the chloridization at the temperature and under the conditions existing in this furnace, it is completely evaporated before any decomposition can take place. The water probably dissolves some salt and thereby brings that salt into more intimate contact with the mineral particles, and, in this manner, aids the chemical action. Aside from improving the physical condition of the ore charge, it can only consume the extra heat units necessary for its evaporation.

The chloridization might be improved if the roasted ore were allowed to remain on a cooling-floor for a few days, but this, of course, would lose the heat desired for the leaching solutions. Probably much of the chloridization is accomplished by the base-metal chlorides formed by the reaction of their sulphates with the salt.

Comparing the results obtained at the Standard plant with those obtained by hypsulphite leaching on the much more difficult ores from Aspen, Colo. (see "Hypo-sulphite Leaching of Silver Ores"), the question arises whether chloridizing roasting

in a standard furnace and under proper conditions, followed by hyposulphite leaching, would not give much better results; such treatment of ore from Creede, Colo., which is similar in character to the Tintic ore, yielded a recovery of over 90 per cent of the silver. Lead and copper are recovered also by this process. The final products obtained are fully as high grade and are marketed in the same manner as the products obtained at the Standard plant. Hyposulphite solutions are non-corrosive and are easily regenerated.

Losses by volatilization at low temperature roasting in a standard chloridizing furnace are not prohibitive, and the volatile chlorides are easily recovered.

Pilot plants, including Holt-Dern furnaces to be followed by brine leaching, have been installed at San Vicente, Bolivia, and at Pulacayo, Bolivia, to replace the hyposulphite leaching that has been in use there for thirty years. The success of this process will hinge on the adaptation of blast-roasting to high sulphur ore. This has been solved, it is stated, by returning a portion of the calcine to the charge bin to be mixed with the crude ore, thereby reducing the sulphide-sulphur content of the furnace charge.<sup>1</sup>

*Manganese-silver Ores.*—Clevenger and Caron<sup>2</sup> have made an exhaustive study of the treatment of manganese-silver ores, which are notoriously refractory. The results of this work may be summarized as follows:

"It appears that in manganese-silver ores of secondary origin, formed at low temperature, the refractory silver mineral is manganite of silver; whereas, if the ore deposition has taken place at higher temperature, silver silicate may also be present."

"Our experience, however, is that, whether or not the manganese present has a fixed ratio to the silver, it is necessary to dissolve all of the manganese; or if reduction is practiced, all the higher oxides must be reduced to manganous oxide in order to obtain the highest recovery of silver. This clearly indicates that in certain of these ores although the silver has no fixed ratio to the manganese, the manganese is directly related to the refractory silver. . . We have found that the refractory silver in the original ore is insoluble in all the common solvents for metallic silver and its salts—that is, cyanide solutions of all concentrations, dilute and concentrated nitric acid, dilute sulphuric acid, salt solution, alkaline thiosulphates, ammonia, mercury, and other reagents. This conclusion harmonizes with all previous work on the problem."

"In the chloridizing roast, as formerly carried out in various types of roasting furnaces, the ore was first given an oxidizing roast, which was followed by the addition of the sodium chloride for chloridizing. During the oxidizing roast the  $MnO_2$  would be dissociated with the formation of the lower oxides  $Mn_2O_3$  or  $Mn_2O_4$ , depending upon the temperature and time of heating. Also, during this stage, a large portion of the amenable silver compounds in the ore would combine with the Mn and  $SiO_2$  to form additional refractory compounds. It is, therefore, not unusual during an oxidizing roast of ores of this class for all of the silver to be converted into refractory compounds where originally there had been only 60 to 75 per cent of refractory silver. On the addition of sodium chloride to the heated ore in an oxidizing atmosphere a considerable proportion of the silver is converted into silver chloride, but the conversion is never complete, as indicated by the subsequent low recovery of silver. It is, therefore, obvious that the conversion would probably be more complete if oxidation could be avoided during the earlier stages of roasting.

"With chloridizing blast roasting, the necessary fuel and salt are mixed directly with the ore, and, after ignition, the air is either blown or drawn through the charge. Under these conditions, during the heating of the ore an excess of carbon is left which



to a greater or less extent reduces the higher oxides of manganese to the lower oxides, even as low as manganous oxide. This condition largely liberates the silver in a finely divided metallic condition which is ideal for chloridization. However, during this first stage, in which the conditions are reducing, no chloridization of the silver can take place at the temperature employed; but later, after the fuel is consumed, the mixture of hot ore and sodium chloride comes in contact with the air, at once giving conditions favorable to chloridization."

This idea has been developed in the Vermaes process<sup>1</sup> in which the finely crushed ore is mixed with organic material and sodium chloride. This mixture is heated to a temperature of 320 to 330°C., after which the ore is cyanided. The organic matter is added for the purpose of breaking up the manganese-silver compounds. The reduction of natural manganese dioxide begins at a temperature of approximately 90°C. in an atmosphere of hydrogen or carbon monoxide. In the dry distillation of organic material, hydrogen, carbon monoxide, and hydrocarbons are readily formed at temperatures of 180 to 200°C., and the reducing gases so formed will react with the higher oxides of manganese, reducing them to a lower oxide—generally to  $Mn_2O_3$ . According to Vermaes, the silver will then combine with the salt to form silver chloride. Since the temperature in this process does not rise above 330°C., all the charcoal resulting from the distillation of the organic material remains unacted upon and finely divided throughout the ore. Vermaes claims there is no loss of gold or silver by volatilization at this low temperature. Clevenger and Caron found a small loss of gold but no loss of silver when conducting the chloridizing roast in a reducing atmosphere at 300°C.; they also found that "the silver is not all present as chloride, a small part being in the metallic state, since decomposition of silver chloride begins in a reducing atmosphere at 300°C." The amount of salt used in this process is 1 to 3 per cent depending on the proportion of silver present in the ore.

The percentage of silver volatilized<sup>2</sup> from manganese-silver ores by the chloride volatilization process is far below that which would be necessary for successful commercial operations.

Conversion of these refractory manganese-silver compounds into silver chloride by wet methods has been attempted by several investigators, but chiefly by Linton.<sup>3</sup> He ground the ore and salt to pass a 100-mesh screen and then agitated the mixture for 24 hr. in a 5 per cent solution of sulphuric acid. The ore pulp was then filtered off, washed, and cyanided. The silver recoveries varied from 60 to 94 per cent. Clevenger and Caron found that the extraction of silver varies as the manganese is dissolved as sulphate, and in order to obtain a high extraction of silver it is necessary to dissolve all the manganese; therefore, the process is amenable only to ores low in manganese and with a gangue insoluble in acid. The use of hydrochloric acid instead of sulphuric acid has yielded high recoveries of silver when followed by cyanidation; free chlorine is evolved when either acid is used. It is difficult, particularly with the higher grades of manganese-silver ores, to filter and completely wash the ore pulp. The manganese sulphate remaining in the residue is an active cyanicide.

**Brine Leaching of Lead Ores.**<sup>4</sup>—In 1916 considerable work was done on the hydrometallurgy of lead at the Bunker Hill & Sullivan mine at Kellogg, Idaho, following an attempt to use the dry chlorine-gas process. It was found that dry

<sup>1</sup> VERMAES, STEFANUS JOHANNES, "Treatment of Refractory Manganese Ores Containing Precious Metals or Silver Alone," U S patent 1234426, July 24, 1917, CLEVINGER, GALEN H and CARON, MARTINUS H., *op cit*, p 34

<sup>2</sup> CLEVINGER, GALEN H and CARON, MARTINUS H., *op cit*, p 30.

<sup>3</sup> LINTON, ROBERT, "Silver Ore Treatment in Mexico," *Jour Chem Met Min Soc of South Africa* 9, (March, 1909), 307; CLEVINGER, GALEN H and CARON, MARTINUS H., *op cit*, p 31.

<sup>4</sup> LYON, D A and RALSTON, O C, "Innovations in the Metallurgy of Lead," U S Bur Mines Bull 157; "Leaching Lead from Carbonate Ores," *Min Sci. Press* (Mar 1, 1919), 277-282; RALSTON, O. C., "Salt in the Metallurgy of Lead," *Trans. A. I. M. E.*, 67 (1917), 634-656.

chlorine gas, acting on lead sulphide, produced lead sulphate and not lead chloride. The fine galena concentrates were, therefore, roasted to the sulphate of lead by the ordinary method and the roasted ore was leached with a strong solution of common salt. This solution was electrolyzed, using sheet-iron anodes. Pure lead was obtained in spongy form with the theoretical consumption of iron. The process seemed feasible with reference to cost and recovery, but, with a smelting plant already in operation and treating all classes of ore, the leaching process was not developed to a commercial scale.

Experimentation by U C Tanton, metallurgical engineer for the Bunker Hill & Sullivan Co, has been continued since that time in perfecting the electrolytic cell, and now a pilot plant has been constructed to treat the tailings from the concentrating mill. The tailings contain considerable siderite or carbonate of iron. They were given an ordinary oxidizing roast to convert the iron into the insoluble oxide and the galena into the sulphate. The calcines were then leached with hot brine containing ferric chloride. The lixivium was passed through a diaphragm electrolytic cell equipped with insoluble anodes. Lead and silver were precipitated on the cathodes, and the chlorine liberated at the anodes was absorbed by the ferrous chloride in solution, regenerating ferric chloride for new lixiviant.

Later development in this pilot plant during 1924-1925 has resulted in further changes in the process. The ore is now roasted at a temperature not exceeding 500°C. in a cylindrical furnace, which is heated electrically by a central core of heat-resisting iron pipe, this obtains a highly oxidizing atmosphere without the contamination of fuel gases. It is proposed to change the source of heat from electricity to oil.

The roasted ore is leached with water to remove the zinc and other soluble sulphates. It is then leached with hot brine from the electrolytic cells, to which some bleaching power has been added. The calcium chloride in the bleaching powder precipitates the sulphuric acid radical from solution as calcium sulphate and thereby obtains an efficient dissolution of the lead. This is followed by a leach with new brine solution. The ore treated contains about 5 per cent lead. The consumption of salt is from 30 to 50 lb per ton of ore.

The lixivium from the leaching vats contains 12 to 15 lb of lead per ton and is sent to the electrolytic cells, these cells are closed for the recovery of the chlorine. The anodes are graphite and are separated from the cathodes by diaphragms. The liberated chlorine gas is passed over lime to prevent it from becoming obnoxious around the plant, this also forms the bleaching powder used in the process. Only the calcium chloride—not the calcium hypochlorite—thus produced, performs any valuable function in the process. The lead is precipitated on a submerged revolving cathode (135 r p m) with a current density of 15 amp per sq ft and at a pressure of 3 to 4 volts. The lead is deposited in a spongy condition and is constantly brushed off the cathode. It is pumped from the bottom of the cells and sent to a filter to separate it from the electrolyte. The lead sponge is melted into bullion and the electrolyte, entirely free from lead, is returned to the leaching vats. Gold and silver are deposited with the lead, but, by using a lower current density, it is possible to precipitate them preferentially from the lead in a highly concentrated product.

This process is in continuous commercial operation at the Bunker Hill & Sullivan Mine.

The Chemical & Metallurgical Corporation of England likewise developed the *Elmore process* for the extraction of lead and silver from lead-zinc concentrates or high-grade complex ores. The ore was given a chloridizing roast with a small amount of salt at a temperature not exceeding 400°C, in order to chloridize the silver only. The roasted ore was then agitated in a series of rubber-lined cones with a saturated salt solution containing 10 per cent sulphuric acid, at a temperature of 100°C. Sul-

phureted hydrogen was given off and lead sulphate was formed. Sulphur dioxide gas was introduced into the last cone to prevent the formation of silver sulphide from the zinc sulphide present. Lead and silver passed into solution and the zinc remained as a sulphide with the gangue. The solution was passed over lead plates to precipitate the silver and then cooled to precipitate the lead as sulphate and chloride. The process was not a commercial success on account of the extreme mechanical difficulty in handling the hot, corrosive, acid solutions on a large scale.

The Combined Metals Reduction Co.,<sup>1</sup> an organization financed by the National Lead Co., erected a plant at Bauer, Utah, in 1925, to treat complex sulphide ores by the Snyder-Christensen process.<sup>2</sup> The ore treated is the very complex middling from the concentrating mill where selective flotation is used on complex ores. This middling product is treated with hot brine acidified with hydrochloric acid, which dissolves the lead and silver sulphides (also oxidized minerals) but does not attack the zinc and copper sulphides. Hydrogen sulphide is evolved which may be used as a precipitant for the silver and lead if desired, but evidently this procedure is not feasible because this gas, at the present time, is sent out of the stack; unless it is utilized eventually it will become a nuisance in large scale operations. It has been found more advantageous to separate the lead chloride by cooling the lixivium than to recover the lead direct from this solution by means of electrolysis or by precipitating on iron. An attempt was made to fuse the lead chloride thus produced and precipitate the lead by the addition of metallic zinc, but no market could be found for the zinc chloride. It is proposed now to smelt the lead chloride with lime and return the calcium chloride to the circuit.

The hydrochloric acid used for acidifying the brine is made in a separate plant so that the sulphates can be eliminated from the lixiviant and thereby secure a high extraction of the lead (compare with the Holt-Dern process described under "Brine Leaching of Silver Ores"). The lixiviant is a nearly saturated solution of salt; the acidity is varied to satisfy the lead content of the ore treated and is maintained at the ratio of 0.5 lb. hydrochloric acid to each 1.0 lb. of lead in the ore; at the end of the leaching operation, the lixiviant should contain 0.5 per cent of free hydrochloric acid. During the leaching operations it is necessary to maintain the temperature of the lixiviant at 95°C, which is near the boiling point. Such a solution is very destructive to any type of leaching vat and to all appliances used in the plant; the materials used in this construction are confined to wood and rubber. The lixivium coming from the leaching vats is said to carry 4 per cent or 80 lb. lead per ton.

The plant was designed for a capacity of 150 to 200 tons of ore per day, but the mechanical difficulties in handling the hot, corrosive, acid brine; in disposing of large quantities of hydrogen sulphide gas; and in making a satisfactory recovery of the metals, have been so great that the process can scarcely be considered past the experimental or pilot plant stage.

An experimental leaching plant, using practically the same process, has been established at Keeler, California, by the Chemical Development & Reduction Co.<sup>3</sup>

The extraction of silver and copper is about 90 per cent respectively.

**Brine Leaching of Copper Ores.**—The use of chlorine in the metallurgy of copper is now confined to the chloridizing roasting of cupriferous cinder from sulphuric acid manufacture. The principal source of this material is pyrite from Spain, which is not only shipped to the United States but to many points in Europe, although other sources of pyrite are also used in quantity.

<sup>1</sup> "Snyder-Christensen Process Works Well at Bauer, Utah," *Eng Min Jn-Press* (July 4, 1925), News Item

<sup>2</sup> U S patent 1549062, August 11, 1925, CHRISTENSEN, N C

<sup>3</sup> DAWSON, C M, "The Experimental Plant of the Chemical Development & Reduction Co.," *Eng Min Jn-Press* (Sept 5, 1925), 383

The practice is essentially the same in the United States and Europe, and also in Japan. The process is more extensively used in Europe and some modifications have been introduced there by Ramén<sup>1</sup> that are known as the Ramenia system. The acid roasters are operated so as to leave a little more sulphur than copper in the cinder. The average copper content is between 2.5 and 3 per cent, and the sulphur is between 3 and 4 per cent. This slight excess of sulphur is desired to get the proper heat of reaction. If not already in fine condition, the cinder or calcine from the acid roasting furnaces is pulverized to pass a 10-mesh screen. For this grade of cinder, 8 to 10 per cent of salt is added. The Scandinavian plants use principally Norwegian pyrite cinders, and these vary widely in both chemical and physical properties. Some of them contain 2 to 6 per cent zinc. The zinc sulphide does not oxidize readily, and consequently the cinder carries a higher percentage of sulphur, which must be compensated with an additional percentage of salt.

The furnaces used are the Wedge type in the United States and the Ramén-Beskow type in Europe. Both types are multiple-hearth furnaces and are usually direct fired on the lower hearth by producer gas or by coal from a fire box.

The Wedge furnace is 20 ft. in diameter and has five hearths. The Ramén-Beskow furnace is essentially of the same construction as the Wedge, but the first and second hearths are separated, making two compartments of the furnace. The combustion gases thus are kept separate from the acid gases from the chloridizing roast. The draft is regulated by fans. The ore mixture on the first hearth is brought to a temperature of about 300°C. by the use of fuel, this is sufficient to start the chloridizing action. From this point the ore passes to the lower hearths successively, and, with the chemical action started, enough heat is generated exothermically to complete the chloridization without extraneous fuel, and there is no danger from overheating or from loss by volatilization.

The coal required in American practice varies from 8 to 12 per cent of the weight of the cinder, depending upon the character of the cinder treated, the furnace conditions, and the quality of coal used. At the Oscarshamn Copper Works, Oscarshamn, Sweden, where the latest improvements of the Ramenia system have been in operation about four (now eight) years, the Ramén-Beskow furnaces are fired with producer gas made from tarry wood. The wood consumed corresponds to about 2 per cent of coal, based on the weight of the cinder. In order to maintain the heat of reaction, they mix a certain amount of green pyrite with the cinder during chloridizing roasting. Since they pay for the sulphur and copper, and sometimes for the iron in cupriferous pyrite, the amount paid for the sulphur thus consumed as fuel makes their actual fuel cost equivalent to American practice, although it is not so published.<sup>2</sup> The temperature is never allowed to exceed 1100°F., or 600°C. Below this temperature there is no loss of copper by volatilization.

The leaching vats are made of wood. Concrete, glazed tile, and acidproof brick have been used for lining vats in the United States, but operation over a period of years has proved that wood is as satisfactory material as any other. In Europe, reinforced concrete is used. Connecting pipes or launders are made of wood and solutions are usually lifted by air-lift pumps, although in Europe wooden centrifugal pumps have proved satisfactory after long service. The filters are built of strips of wood in the form of lattice work. These are covered with prairie grass or similar material and on top of this is placed several inches of wet leached cinder.

<sup>1</sup> OSTMAN, N., Chloridizing and Leaching as Practiced in Sweden. *Eng. Min. J.* (Mar. 5 1921), 417-422.

<sup>2</sup> Coincident with this development may be mentioned a modified construction of the Wedge furnace for autogenous blende roasting. It is 25 ft. in diameter and has eight hearths. The essential feature of the furnace is the arrangement for by-passing the roasted ore between the several hearths in order to obtain a desired distribution of the ore preheated in the upper part of the furnace, among the lower reaction chambers. INGALLS, W. R. *Mining Met.* December 1922.

In American practice, the hot ore from the roasting furnaces is dumped directly into the vats. Some plants in Scandinavia experienced considerable trouble with hard lumps forming in the chloridized ore, due to the formation of anhydrous sodium sulphate. Ramén overcame this difficulty by designing a "preleaching machine," in which a thin layer of the hot chloridized ore from the roasting furnaces is evenly sprayed with sufficient water to permit the crystallization of the sodium sulphate, and the moistened ore then remains in a pulverulent condition. This machine runs continuously and the preleached ore is conveyed to storage bins, where it is picked up by a grab bucket and placed in the leaching vats. Considerable steam is generated by this operation, which is condensed and furnishes hot water for leaching.

The gases from the chloridizing roasting furnaces pass through scrubbing towers. These are built of wood on a brick or concrete base. They are loosely filled with any inert material and sprayed with water at the top. They prevent the noxious gases from escaping into the atmosphere and becoming a nuisance; they also condense and recover the acid fumes. The hot, acid water from these towers is used for leaching purposes. In the Ramenia process the acidity of this water is kept at 15 to 24 g. of HCl per liter, which insures the extraction of all soluble copper.

The leaching vats can be made any size, but usually hold about 100 tons. The ore bed is 3 to 4 ft. deep. By utilizing the hot ore, hot, acid water from the scrubbing towers and hot water from other sources mentioned, all leaching is done with hot solutions which average between 30 and 40°C. on leaving the vats and contain about 25 g. of copper per liter.

In Europe, the time of leaching ranges from 35 to 45 hr. under the ordinary system, but by using a "preleaching" machine this is reduced to about 24 hr. In America, where the copper extraction is usually made by the acid makers, the acid roasting furnaces are better controlled and the cinder is in better physical condition for chloridizing roasting. Under these favorable conditions leaching can be completed in less than 10 hr. in the ordinary manner, and even with unfavorable conditions the time seldom exceeds 24 to 36 hr. After washing, the cinder is removed from the vats by grab buckets, or by other means, depending upon local conditions. The copper remaining in the leached cinder is not over 0.1 per cent and is usually less than that. This gives an average extraction of about 97 per cent.

The copper is recovered from solution by precipitation on scrap iron. This is done in the usual "boxes" or launders, which yield a precipitate containing about 70 per cent copper, or in "tumbling barrels" or drums which yield a precipitate containing 85 to 90 per cent copper. The advantage of the revolving drum is that the precipitation is done quickly by agitation, and the iron is kept clean, so there are no basic iron salts formed to contaminate the copper precipitate.

The leached cinder is known as purple ore, or "blue billy." If the original pyrite was commercially pure, the purple ore contains from 55 to 68 per cent Fe, and not over 0.01 per cent P, 0.2 per cent S, and 0.1 per cent Cu. In 1891, Bird, of England, discovered that this material could be pressed and burnt into strong briquettes without any binder. This idea was developed commercially for fine iron ores, first by Anderson in America in 1888, and later by Grondal in Sweden in 1896. The purple ore is pressed by slow compression into briquettes and heated in tunnel furnaces to a temperature of 1450°C. At this temperature practically all the sulphur is removed and the briquette is sintered. In this condition it makes a desirable iron ore, which assures a saving of 8 per cent coke in the blast furnace and frequently increases the capacity 30 per cent compared with ordinary iron ore. It is extensively used in Europe and Japan.

Under the circumstances it is difficult to arrive at the actual average cost of producing copper by this process, since the recovery of copper is only one of three phases in the treatment of the original pyrite. In America, the copper-recovery plant

is an adjunct to the acid plant. The purple ore is nodulized and sold to the iron smelters. The profits derived from the copper and iron may be deducted from the cost of acid making. In Europe, the cupriferos cinder is bought from the acid maker and the recovery of the copper is expected to pay all the expense of producing a desirable iron-ore briquette, which is sold to the iron smelter. Greenawalt<sup>1</sup> gives the cost of producing copper by this process in the eastern United States, previous to 1912, at 5.19 cts. per pound. This is based on the treatment of pyritic cinder containing 2.27 per cent copper and 2.28 per cent sulphur. He estimates the cost of treating the same grade of copper ore in the western United States by the same process at \$2.96 per ton.

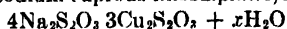
**Brine Leaching of Zinc Ore.**—Chloridizing roasting and water or brine leaching, as described under copper ore, have been successfully applied to zinciferous cinder within the last few years for the purpose of extracting zinc in solution for the manufacture of lithopone.<sup>2</sup> The treatment of zinc ores will be further discussed under dry chlorine-gas processes.

**Hyposulphite Leaching of Silver Ores.**—Hyposulphite (sodium thiosulphate) leaching came rapidly into favor in the United States after 1885; it was already well established in Mexico. It reached the zenith of its popularity between 1886 and 1893 and was practically abandoned as a metallurgical process at the end of that period, due to the demonetization of silver in the United States and the general closing down of silver mines. The process is still used to a limited extent in South America and Mexico.

Chloridizing roasting necessarily precedes the leaching, and the chloridized ore is washed with water to remove the base-metal chlorides before applying the hyposulphite solution. This process is, therefore, closely related to brine leaching. It is essentially a process for silver ores and the base metals are considered a nuisance. Silver is recovered as a sulphide from the hyposulphite solution by precipitating with sodium sulphide and the hyposulphite is thereby regenerated.

When the chloridization of the silver is low, due to inefficient roasting, the extraction is low. Zinc sulphide acts in an unexpected manner. At the Holden Lixiviation Works in Aspen, Colo., the ores carried about 2 per cent zinc, and a zinciferous pyrite was used as a source of sulphur. The short period of roasting in the Stetefeldt furnace and four days of heap roasting on the cooling-floor did not oxidize the zinc sulphide, although the chloridization of silver was satisfactory. As soon as the chloridized ore was placed in the vats and leached with water, 20 to 40 per cent of the silver reverted to the sulphide, due to precipitation by the unoxidized zinc sulphide in the ore.<sup>3</sup> By roasting with a clean pyrite, this difficulty was largely removed.

These defects in hyposulphite leaching were overcome to some extent by E. H. Russell,<sup>4</sup> who discovered that a little copper sulphate added to the hyposulphite solution formed a double salt of sodium cuprous thiosulphate, having the formula



This salt has the power of dissolving sulphide of silver by forming sodium silver thiosulphate and cuprous sulphide.

<sup>1</sup> GREENAWALT, WILLIAM E., "The Hydrometallurgy of Copper," p. 267, New York and London, 1912

<sup>2</sup> OSTMAN, N., *op cit*, p. 421

<sup>3</sup> MORSE, W. S., "The Effect of Washing with Water upon the Silver Chloride in Roasted Ore," *Trans. A. I. M. E.*, 25 (1895), 587-594

<sup>4</sup> STETEFELDT, C. A., "Working of Silver Ores by the Leaching Process," *Trans. A. I. M. E.*, 12 (1884), 291-295; "The Lixiviation of Silver Ores with Hyposulphite Solutions, with Special Reference to the Russell Process," New York, 1884, 2nd Ed., 1893. DAGGERT, LLESWORTH, "The Russell Process in Its Practical Application and Economic Results," *Trans. A. I. M. E.*, 16 (1888), 362-495

The solution thus formed is known in the Russell process as "extra" solution and follows the "regular" or "ordinary" hyposulphite solution in the leaching operations. By the use of this solution the extraction is restored to the extent of the original chloridization of the silver and even beyond that point.

The three lixiviants used in the Russell process are, therefore: (1) wash water (brine), to remove the soluble salts, (2) "regular" solution of sodium thiosulphate, (3) "extra" solution of sodium cuprous thiosulphate.

The ore treated by the Russell process at Aspen, Colo.,<sup>1</sup> in 1891-1893, affords a good example of a troublesome ore to treat by hyposulphite leaching. It had the following composition:

Ag, 27.92 oz. per ton, Pb, 2.28, SiO<sub>2</sub>, 21.66, BaSO<sub>4</sub>, 20.92, CaO, 11.00, MgO, 4.24, Fe, 10.02, Zn, 2.85, Cu, 0.16, S, 8.10 per cent.

The ore feed to the roasting furnace was crushed to pass a 30-mesh screen, this is common practice for hyposulphite leaching.

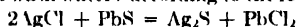
The chloridization of the silver in the Stetefeldt furnace was 43.5 per cent, it was a little higher in the fumes and dust chambers, making the average chloridization 52.5 per cent by the direct roasting operation. The roasted ore was piled on a cooling-floor and allowed to remain an average of 102 hours, during which time the chloridization of the silver increased to 79.0 per cent.

The respective lixiviants mentioned above extracted the percentages of silver given below, as calculated from the average daily assays:

	PER CENT
Wash water (brine)	14.56
"Regular" solution	44.21
"Extra" solution	27.98
Total extraction	86.75

The actual extraction during the entire period of operation, based on the silver recovered and paid for, was 94.21 per cent of the silver in the roasted ore and 85.58 per cent of the silver in the raw ore. The volatilization and dust losses were 9.16 per cent of the silver which would be fully recovered in present day practice.

Considerable lead was dissolved by the wash water, which was precipitated with the silver as a sulphide by means of sodium sulphide. This gave a low-grade product that was expensive to refine. It was found by W. S. Morse, manager of the Aspen plant, that this precipitate, containing lead sulphide, could be utilized as a precipitant for the silver in subsequent wash waters according to the following reaction:



This raised the grade of the final product and reduced the refining cost.

Subsequently, lead was removed from the wash water and the "regular" solution by precipitating with sodium carbonate. Lead is preferentially precipitated in this manner before the lime and magnesia.

The silver sulphide precipitate from the hyposulphite solutions was eventually refined at the plant by dissolving in hot concentrated sulphuric acid and precipitating the silver in metallic condition on copper.

Local conditions sometimes demand a variation from standard methods. In Bolivia,<sup>2</sup> where the metallurgical problem involves the treatment of silver-bearing tin ores, certain modifications in chloridizing roasting have been found necessary. The chief gangue minerals of the ore are pyrite and quartz. The silver occurs in

<sup>1</sup> MORSE, W. S., The Lixivation of Silver Ores by the Russell Process at Aspen, Colo., *Trans. A. I. M. E.*, **25** (1895) 137, 146, 993, 997.

<sup>2</sup> SCHNEIDER, M. G. F., Roasting and Chloridizing of Bolivian Silver-tin Ores, *Trans. A. I. M. E.*, **64** (1920), 676-698.

tetrahedrite, jamesonite, stibnite, cylindrite, and other complex sulphantimonial minerals, which are notoriously difficult to treat by any process other than smelting. Most of the tin is present in the form of impure cassiterite, although it is sometimes present as stannite associated with the above-named minerals.

At the present time the ore is crushed dry, given a chloridizing roast, and leached with water and hyposulphite solution or with brine to extract the gold, silver, and copper. The tailings are concentrated for tin, with or without regrinding.

The percentage of silver that can be chloridized is not directly proportional to the silver content of the ore. Tailings from any grade of ore will contain from 5 to 9 oz., which cannot be extracted by any known commercial solvent, even though only a small proportion of this silver is in the form of sulphide.

The average grade of ore treated assays about 35 oz. silver per ton. The ores contain from 25 to 35 per cent sulphur, most of which must be removed by preliminary roasting before adding salt for chloridizing. Fuel is expensive in Bolivia, so it is necessary to utilize as much as possible the heat developed by the desulphurizing roast.

A peculiarity of this ore is the loss of over 30 per cent of the silver by volatilization and in flue dust during desulphurizing roasting in a McDougall furnace, which, added to the loss from insoluble silver, makes the loss over 40 per cent. Similar but lower losses occur in hand-rabbed reverberatory furnaces. These losses can be fully recovered by means of a Cottrell precipitator, but an analysis of this product indicates that the losses are due largely to antimony, and no satisfactory process has been developed for treating it to recover the silver.

A satisfactory furnace has been finally developed in a modified form of the Edwards-Merton straight-line furnace, which has five hearths and is divided into three compartments by means of doors or dampers to control the draft. By the time the ore reaches the fifth or last hearth, it is ready for chloridization and the damper is closed, cutting off that hearth from the rest of the furnace. The necessary amount of salt is added and the charge is chloridized in about 15 min. The chloridized ore is discharged in another 15 min. and the process repeated. This makes the operation of the furnace intermittent to some extent, but the volatilization and dust losses are greatly reduced.

Only 3.3 per cent of salt is used for chloridizing and no extraneous fuel is required.

The chloridization of the ore is simple and quick if salt is added at the correct stage of the roast.

Samples taken every 10 min. from the chloridizing hearth for an hour after the first 15 min. show no improvement in the chloridizing by prolonging the process.

The loss of silver during roasting is 1.5 per cent. The loss as insoluble silver is 12.2 per cent, making a total recovery of 86.3 per cent. The cost of roasting only is about \$1.12 per ton.

Other mining companies in Bolivia have continued to use the Patera, or hyposulphite leaching process, as the most economical for the treatment of their ores.<sup>1</sup> "The lack of local lead or copper smelters, and the high freight charges to the outside, prohibit the shipment of any but high-grade ores or products. Cheap salt, in unlimited amount, is available from the various closed basins of western Bolivia. Numerous semi-active volcanoes supply sulphur. Lime is also locally obtainable. Hence the Patera process, producing high-grade silver sulphides, has continued to prove an economical treatment for many high-sulphur ores that require little fuel to roast."



## CHLORIDE VOLATILIZATION PROCESSES

**Pohlé-Croasdale Volatilization Process.**<sup>1</sup>—Pohlé and Croasdale discovered, by raising the temperature of chloridizing roasting to 1050°C., that gold, silver, copper, and lead can be commercially volatilized as chlorides from their ores and the metals recovered from the fumes. By charging the ore, salt, and sulphur mixture as quickly as possible into the hot zone of the furnace, volatilization begins at about 750°C. and is completed within 30 to 60 min. The roasting atmosphere must be kept highly oxidizing. The process is continuous and the ore is commercially devoid of value as it discharges from the furnace.

The furnace used for this process is a regular cement kiln, 100 to 125 ft. in length, fired in the usual manner.

The chemical reactions involved are the same as those given for chloridizing roasting in the preceding section. There should be a strict adherence to the proportions there stated. The ore and salt are crushed to pass a 20-mesh or 0.75-mm. screen.

The process is applicable to all ores in which the metals do not occur in native or metallic condition, regardless of the gangue constituents. Basic ores are preferable because they do not fuse or sinter at the temperature of the roast. Siliceous ores work almost as well. Neutral ores are least desirable when the acid and base gangue constituents are in such proportions as to form a fusible combination with the salt at the furnace temperature. In such cases calcium chloride may be used in place of common salt, or lime may be added to the charge in sufficient quantity to raise the fusion point.

Common salt is the usual source of chlorine on account of its cheapness, but in some instances it has been found desirable to use calcium chloride wholly or in combination with the salt. Sulphur is usually a necessary constituent of the charge, although with some ores the silica or carbonic acid seems to take its place in the chemical reactions.

Gold is easily volatilized, but in what form has not been definitely determined. It was generally supposed that gold trichloride was formed at low temperatures, and this was decomposed into metallic gold and chlorine at temperatures below 300°C. If this is true, the metallic gold formed from the vapors is probably colloidal and is carried out of the furnace in that form with the gases. Rose<sup>2</sup> states that when gold is heated in chlorine at atmospheric pressure trichloride of gold is formed, which volatilizes at all temperatures above 180°C. up to and beyond 1100°C. Other metallurgists<sup>3</sup> think that gold forms a double chloride with salt, or other metallic chlorides, and volatilizes in that form. The theory of a double chloride seems more probable.

Silver is less easily chloridized and volatilized than any of the common metals. It seems to be extremely sensitive to atmospheric conditions in the furnace and may be affected by the gangue constituents in the ore.<sup>4</sup> Silver chloride melts to a thin liquid at about 451°C.<sup>5</sup> before it volatilizes, which probably accounts for its sluggish volatilization. It is much more easily volatilized in the presence of other metallic chlorides, which would indicate that it volatilizes as a double chloride.

Lead is the most easily volatilized of all the metals as a chloride and the chloride is easily formed by chloridizing roasting. With some ores, sulphur is not necessary

<sup>1</sup> CROASDALE, STUART, "Volatilization of Metals as Chlorides," *Eng Min. J.* (Aug 29, 1903), 312-314; U. S. patent 741712, Oct 20, 1903

<sup>2</sup> ROSE, SIR T. K., "Metallurgy of Gold," pp 61-63, London, 1915

<sup>3</sup> STETEFELDT, C. A., *op cit.* p 340

<sup>4</sup> U. S. Bur Mines Bull 211, p 45.

<sup>5</sup> VARLEY, THOMAS, Superintendent, Utah Station, U. S. Bureau of Mines, Salt Lake City.

in the chloridizing of lead minerals, and some experiments<sup>1</sup> have shown that volatilization can be accomplished more successfully without it.

Copper is readily volatilized as cupric chloride and as cuprous chloride. Cuprous chloride is the more stable at high temperatures. Some oxychlorides may be formed, but not to any large extent.

Zinc is volatilized according to the sulphur content of the ore. In oxidized ores, lead, silver, copper, and gold can be volatilized preferentially, leaving the zinc in the gangue for subsequent treatment. If complex sulphide ores are roasted so that the sulphur content is only sufficient to combine with the other base metals, these metals can, in a similar manner, be preferentially separated from the zinc by the volatilization roast, but if any excess of sulphur over the amount specified is left in the ore after the preliminary roast, zinc will volatilize with the other metals in proportion to the excess of sulphur present in the charge.

Little information is available concerning the chloridizing action on the gangue materials. Silica acts as an acid and decomposes salt, with the liberation of chlorine at high temperatures. Iron chlorides are formed from the sulphides, but they quickly decompose to the oxide and very little of the iron is volatilized.<sup>2</sup> Aluminum is not volatilized as a chloride from its oxide in an oxidizing atmosphere (see p. 1181). Calcium and magnesium may be volatilized to some extent as chlorides,<sup>3</sup> but they in no way interfere with the volatilization and recovery of the other metals.

The metallic chlorides are driven from the ore in the form of vapor and they condense as colloidal particles of fume. Each particle is surrounded with an adsorbed film of air or furnace gas, which prevents coagulation and collection by any other means than electrical precipitation.<sup>4</sup> The fume particles thus enveloped will pass untouched through water or any form of scrubbing device. The electrical stresses set up in the Cottrell precipitator break up these gas envelopes and permit the coagulation and recovery of the fumes. Bag filters of textile material will make a high recovery, but are difficult to operate, owing to the corrosive nature of the fumes and gases.

The metals are recovered from the precipitated fume by the substitution of one metal for another in an aqueous solution or by the electrolysis of the fused chlorides. Where the metals in the fume consist only of copper, silver, and gold, or lead, silver, and gold, the fumes are reduced to a bullion by heating with lime and carbon. The calcium-chloride slag can be utilized in place of salt to chloridize new ore.

Several small plants have been operated in the United States, but they were equipped with furnaces ranging from 25 to 60 ft in length. These furnaces were too short to complete the volatilization when operating at commercial capacity. A full-sized plant was operated by the Blaisdell Coscoticlan Syndicate,<sup>5</sup> Pachuca, Hidalgo, Mex., on patio tailings. Their furnace was a kiln 125 ft long and 8 ft in diameter, lined with 9-in. concrete clinker brick. The fuel consumption was 12 gal of 18,500 Btu oil per dry metric ton and this without preheating the air or ore, or using any insulation. The recoveries were well over 90 per cent on the gold, copper, and mercury, 100 per cent on the small amount of lead, and 75 per cent on the silver, which was considered good on this class of material. No advantage was found by using calcium chloride, but 5 per cent of lime was necessary to reach the proper finishing

<sup>1</sup> RALSTON O C 'Salt in the Metallurgy of Lead, *Trans A I M E* 87 (1917) 639-641 VARLEY, THOMAS, U S Bur Mines Bull 211 footnote p 19

<sup>2</sup> Nickel volatilizes as a chloride to a greater extent than iron and it might be possible to recover nickel in this manner. If oxidized by a preliminary roast, nickel will remain in the gangue and it is possible preferentially to volatilize copper from nickel by the chloridizing roast.

<sup>3</sup> MORSE W S 'Lixivation of Silver Ores by the Russell Process at Aspen, Colo.' *Trans A I M E*, 28 (1895), 997

<sup>4</sup> BANCROFT W D *Applied Colloidal Chemistry*, pp 21, 22, 201, 300, New York and London, 1921

<sup>5</sup> U S Bur Mines Bull 211 pp 83, 84

temperature. The property was forced to cease operations on account of the low price of silver.

It is expected that a commercial plant will be put into operation in the near future by the Western Metallurgical Co. of Los Angeles. It has been found advantageous to add the salt at successive intervals during the roast, rather than all at once with the ore. In doing so the fusing temperature of the charge is maintained at a higher point, and the chloridization, consequently the volatilization of the metals, is considerably increased. It is also proposed to preheat the ore to the volatilization temperature in a separate furnace before adding the salt. The salt and the hot ore will then be fed into another furnace, which can be maintained at the volatilization temperature with a comparatively small amount of fuel and the chloride fumes can be sent to the Cottrell treaters less contaminated with combustion gases and other inert material. Certain advantages have also been found in passing the ore charge through the furnace concurrently with the combustion gases, instead of countercurrently as is now practiced, but this system has not yet been developed commercially. The total cost of ore treatment by this process has been conservatively estimated not to exceed \$3 to \$3.50 per ton.

Maier<sup>1</sup> has discovered that lead and zinc are readily and almost completely volatilized as chlorides when their oxides (in ores) are heated, without reducing agents, in a current of chlorine gas at temperatures ranging from 500 to 750°C. The chlorides of both metals are volatilized and easily condensed in a relatively pure condition; the principal impurity is calcium chloride—and magnesium chloride would probably volatilize also if present in the ore. Iron and aluminum chlorides are decomposed at low temperatures and do not volatilize to any appreciable extent. This research work has been carefully done and is suggestive of further application of the process.

*Oxide Volatilization.*—Corollary to chloride volatilization is the oxide volatilization process, developed by the Chief Consolidation Mining Co.,<sup>2</sup> at Eureka, Utah. Ores from this mine vary from entirely oxidized ores to ores showing only slight oxidation, and from nearly self-fluxing ores to highly infusible ores. The average ore has approximately the following composition: Au, 0.055 oz. per ton; Ag, 25.2 oz. per ton; Pb, 6.0; Zn, 4.6; Fe, 7.0; "Insoluble," 63.8; S, 1.8; and CaO, 2.6 per cent. Smelting and freight charges were high, so the company began its metallurgical research in 1916 to develop a method of ore treatment at the mine, principally along the lines of mechanical concentration and chloride volatilization. This work resulted in the construction of a concentration and volatilization plant, designed to treat 250 tons of ore per day; the plant was started in May, 1925, and has been in continuous commercial operation since that date.

All the sulphide minerals and some of the lead carbonate are recovered by gravity concentration and flotation; this likewise removes all the easily fusible or slag-forming constituents from the gangue. The tailings from the concentrating plant carry 0.035 oz. Au per ton; 11.4 oz. Ag per ton; and 4.7 per cent Pb. These tailings are filtered and then dried by the hot gases from the volatilization furnace in a Ruggles-Coles rotary dryer, 7.5 ft. in diameter and 60 ft. long. An indirect-heat type of dryer is used to avoid contamination of the fume-bearing gas.

The dried tailings go direct to the volatilization furnace, which is the regular cement kiln type, 10 ft. in diameter and 80 ft. long, and is fired with pulverized coal.

<sup>1</sup> MAIER, CHARLES G., "Possibilities of Dry Chlorination of Oxidized Zinc Materials," *Eng. Min. Jn.-Press* (January 13, 1923), 51.

<sup>2</sup> PARSONS, ARTHUR B., "Chief Consolidated Starts Novel Reduction Plant," *Eng. Min. Jn.-Press* (Oct. 11, 1924), 582; BARBOUR, PERCY E., "The New Utah-Idaho Metallurgy," *Min. Met.* (August, 1925), 365; WIGTON, G. H., "The Chief Consolidated Volatilization Process and Mill," *Trans. A. I. M. E.* (September, 1925), *Min. Met.* (August, 1925), 444.

Volatilization experiments were started by using 10 per cent salt, but this produced a fusible slag at temperatures below the point at which a satisfactory volatilization of the silver could be obtained. Reduction of the percentage of salt permitted the raising of roasting temperatures which thereby increased the volatilization and recovery of the silver, until, finally, the use of salt or other chlorides was discontinued entirely and the furnace temperature was raised to 1400°C., at which point the gold, silver, and lead are almost completely volatilized. These results have been duplicated in practice and the elimination of chlorine permits the use of bags for the recovery of the volatilized fume. The calcines discharging from the volatilizing furnace, carry only Tr. Au; 1.2 oz. Ag per ton; and 0.2 per cent Pb, thereby showing a recovery of nearly 100 per cent of the gold, 90 per cent of the silver, and over 95 per cent of the lead, since the recovery of fume by means of the bag-house is practically complete. The recovered fume assays 0.3 oz. Au per ton; 64.0 oz. Ag per ton; and 27.8 per cent Pb. The capacity of this furnace is 7 tons of tailings per hour, and the consumption of coal is about 30 per cent of the furnace feed. The tailings go to the volatilizing furnace without regrinding and will all pass a 20-mesh or 0.75-mm. screen.

Two curious analogies have developed between chloride and oxide volatilization: (1) Accretions of ore occur in the preheating zone of the volatilizing furnace, up to a temperature of about 1100°C., in spite of the fact that no salt or other chlorides are used in the ore feed, but, at higher temperatures these accretions do not exist. They are not slagged accretions, such as rings in cement kilns, but consist of unfused particles of quartz (the principal gangue) loosely bound together by a slight fusion of the other gangue constituents; they do not occur in definite rings, as in cement kilns, but occupy the entire preheating zone. These accretions are removed periodically by means of a water-cooled plow mounted on the end of a water-cooled bar, 86 ft. long, which has a direct-current crane motor and gears mounted on the other end; the gears run on a stationary steel rack mounted on each side of the bar. With this plow, longitudinal trenches can be cut through the accretions when necessary and a clean furnace maintained. The actual plowing operation requires about 20 minutes. (2) As ordinarily operated, that is, passing the feed concurrently with the furnace gases, considerable trouble was experienced with the large amount of flue-dust that passed over with the fume and required retreatment. The ore now is passed concurrently with the gases and, consequently, is fed at once into the hottest part of the furnace; the quick heating softens the ore so that there is almost no dusting. The volatilization is about the same, and the fume carries only about 15 per cent silica. The accretions occur, also, near the end of the furnace where they can be removed more easily. The advantage of getting the ore feed quickly into the hottest zone of the furnace was observed by Croasdale<sup>1</sup> and by all subsequent investigators of chloride volatilization. The Western Metallurgical Co. observed certain advantages in passing the ore feed concurrently with the gases (see preceding section on chloride volatilization).

**Volatilization Processes for the Production of Aluminum Chloride and Aluminum.**—Aluminum was first commercially produced by the Deville process<sup>2</sup> or its modifications. The process consisted of heating alumina and carbon in a retort in an atmosphere of chlorine gas. Aluminum chloride volatilized and was recovered by condensation. In later practice, salt was added to the retort and the double chloride of sodium and aluminum was formed and recovered in the same manner. Metallic aluminum was produced by reduction of this salt with metallic sodium. This process was abandoned a number of years ago as a

<sup>1</sup> "Volatilization of Metals as Chlorides," *Eng. Min. Jn.* (Aug. 20, 1903), 312-314.

<sup>2</sup> RICHARDS, JOSEPH, W., "Aluminum," 3rd ed. (new addition preparing), Philadelphia.

source of aluminum, but anhydrous aluminum chloride may assume considerable importance in the petroleum industry.

Since most of the methods for producing aluminum chloride involve the use of chlorine gas in conjunction with volatilization, the subject will be discussed more fully under Dry Chlorine-gas Processes, (p. 1183). There are, however, several methods proposed which are strictly volatilization processes. One is that of Booth and Marshall,<sup>1</sup> in which aluminum silicate (clay or feldspar) or aluminum sulphate (alunite) is mixed with calcium or magnesium chloride and heated in an electric furnace to a temperature of 1300°C. An alkaline-earth silicate is formed and aluminum chloride is recovered by volatilization and condensation.

Another method is proposed by Burgess.<sup>2</sup> He mixes aluminum carbide with an anhydrous chloride of an element below aluminum in the electrochemical series and ignites the mixture. The reaction begins at 380°C. and is exothermic. The aluminum chloride volatilizes and is recovered by condensation. Lead chloride and silicon tetrachloride are suggested as the cheapest chloridizing agents for the aluminum carbide.

Ravner and Goldschmidt<sup>3</sup> propose using minerals of the feldspar group as a source of alumina, because they contain from 25 to 36 per cent alumina and very little iron. When mixed with carbon they will react to form aluminum chloride in the same manner that pure alumina and carbon react, and at the same temperatures.

Wolcott<sup>4</sup> proposes using oil shale, bituminous shale, and bone coal as raw materials for the production of aluminum chloride since the reducing agent and the aluminiferous material are already most intimately blended and ready to react. The only difficulty is that the alumina and the carbon seldom exist in the proper proportions but, with low-grade coals, the excess of carbon is utilized as fuel for the process. This material is roasted with salt and the aluminum chloride is volatilized and recovered as fume.

### WET CHLORINE-GAS PROCESSES

The Plattner process has been, until recently, in constant use since it was first proposed by Plattner in 1851. It is applicable only for the recovery of gold and for a long time it was used principally for the treatment of concentrates from free-milling ores. The operations were, therefore, conducted on a small scale. The pyritic concentrates were roasted "dead" in a hand reverberatory furnace and then placed in a vat and leached with water saturated with chlorine gas. Owing to the difficulty in handling chlorine gas in this manner, the vat was replaced by a lead-lined iron barrel having a capacity of about 1 ton of ore. Water, bleaching powder, and sulphuric acid were added to the ore in the barrel in such proportions as to form a thin pulp and to generate a slight gas pressure when the barrel was sealed and the charge agitated. The chlorination of the gold was completed after the barrel had been revolved for a few hours. The charge was then dumped into an open vat provided with a sand filter, and washed with water. The gold was precipitated by ferrous sulphate, collected, and melted into bullion.

In 1894 the process was first applied to crude ores from Cripple Creek, Colo. There was no change in the process except to conduct it on a larger scale. The ore

<sup>1</sup> U S patents 1302043 to 1302046 Sept. 27, 1921, BOOTH, H S. and MARSHALL, G. G.

<sup>2</sup> U. S. patent 1321281, BURGESS, LOUIS, Nov. 11, 1919

<sup>3</sup> U S patent 1302852, May 6, 1919, RAVNER, OBYTKIN, and GOLDSCHMIDT, VICTOR M

<sup>4</sup> English patent 160750, Canadian patent 217051, U S patent pending, WOLCOTT, E R

was crushed to pass a 12-mesh or 1.5-mm. screen and roasted in a mechanical furnace. The lead-lined chlorination barrels were enlarged to 10 tons capacity and were provided with perforated lead filters inside. The chlorination was done under pressure with bleaching powder and acid as before; 12 lb. of bleaching powder and 24 lb. of acid were required per ton of ore. The barrels were revolved 2 or 3 hr. and then stopped with the filter at the bottom. A valve was opened under the filter and the leaching and washing were done in the barrel. The tailings were discharged directly from the barrel to the dump. In some instances the gold was precipitated from solution by filtering through charcoal. After a certain time the charcoal was burned and the gold-bearing ashes melted into bullion. Generally, the gold was precipitated by means of sulphureted hydrogen and melted into bullion by fluxing this precipitate. In later practice on Cripple Creek ores, the chlorine was generated by the electrolysis of salt and was absorbed by water as it passed through scrubbing towers 30 in. in diameter and 30 ft. high, made of ordinary glazed sewer pipe. From the towers the saturated solution of gas was pumped into lead-lined storage tanks and then run into the chlorination barrels as needed. The agitation of the charge produced sufficient gas pressure. The rest of the process remained the same as before.

The treatment of Cripple Creek ores by this process continued until 1911, when it was finally supplanted by the cyanide process. During its operation 2,046,223 tons of ore were treated at an average cost of \$2.34 per ton. The tailings averaged 0.063 oz. per ton and the average recovery of gold was 93.23 per cent.

A few chlorination plants continued to treat pyritic concentrates in California up to the time of the World War, but this marked the close of the chlorination process in the United States and it is doubtful if it will ever be revived. It may still be used to some extent in Australia. It is not adapted to ores containing any free basic gangue, owing to the excessive consumption of chlorine. It has been replaced generally by the cheaper and more adaptable cyanide process.

**Vanadium Ores**—Early in 1924, Dr Saklatwalla, research chemist for the Vanadium Corporation of America, developed a process for the extraction of vanadium and some of the rarer metals from vanadium ores by the use of chlorine gas in cold solution. Details of this process are not available. See foot note, p. 1164.

## DRY CHLORINE-GAS PROCESSES

**Chlorine Production.**—With the development of electrolytic processes for the production of caustic soda and chlorine from salt, and with modern methods for drying, liquefying, and transporting chlorine in a liquid state, this element has become a cheap commodity available for many uses and capable of considerable development metallurgically. The actual continuous working capacity for chlorine production in the United States at the present time is about 300 tons per day, which does not include the chlorine made and used in the same plant. The normal consuming capacity is about 180 tons per day. The 120 tons excess producing capacity is the result of war preparation and is now idle.<sup>1</sup>

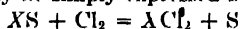
**Malm Process for Complex Ores.**<sup>2</sup>—This process is a development of the Baker-Burwell process described on page 1157. It is adapted to low-grade complex sulphide ores. The ore is crushed on the average to pass a 0.75-mm. screen. The dry ore is fed into a tube mill countercurrently with a stream of dry chlorine gas. The tube mill is divided into three compartments and is not lined. No grinding is done in the tube mill, but a few pebbles are added to keep the charge

<sup>1</sup> BRALLIER, P. S., "The Chlorine Industry in the United States," *Chem Met Eng.* (May 14, 1923), 846-849.

<sup>2</sup> IONIDES, S. A., "The Dry Chlorination of Complex Ores," *Min. Sci. Press* (May 27, 1916), 781-787.

from forming into lumps. Most of the chlorination is done in the compartment at the discharge end where the chlorine gas enters. The central compartment is arranged so as to be heated on the outside of the shell if necessary to start chemical action or to keep chemical action alive if the ore contains little sulphur. The temperature in the tube mill is kept near  $70^{\circ}\text{C}$ , which is still lower than that used in the Baker-Burwell process. About 50 per cent of the chlorination is done in the tube mill, or enough chlorine is admitted here to chloridize all the recoverable metals. If complete chlorination is attempted in the tube mill, the temperature of the charge has to be raised above the melting point of the free sulphur present and the charge becomes sticky.

The chemical reactions may be simply expressed by this equation



Very little sulphur chloride is formed, and if the charge is kept free from moisture no hydrochloric acid is formed. The ore discharges from the tube mill into a multiple-hearth furnace, where the temperature is raised by direct firing but is not allowed to go higher than  $400^{\circ}\text{C}$ . This decomposes the iron chlorides and converts most of the iron into the oxide. The chlorine liberated is absorbed by fresh sulphide ore, which is continually circulated on the two upper hearths of the furnace. The tube-mill discharge is delivered only on the four lower hearths where the chlorination is completed.

From the furnace, the chloridized ore is discharged into an agitator filter, where it is first washed with mill solution which contains the soluble metallic chlorides from previous charges. These are principally chlorides of iron, zinc, and copper. This mill solution dissolves all the metallic chlorides, except the lead chloride and sulphate. The mill solution is followed by a wash of steam, which cleans the charge of soluble metallic chlorides with a minimum amount of water. The wash waters go to storage to build up new mill solution. The ore is then leached with a hot saturated solution of common salt which dissolves the lead salts. This solution is conveyed to a separate tank, where it is allowed to cool and the lead chloride crystallizes out. The lead chloride is collected, fused, and electrolyzed for the recovery of lead and chlorine. The anode is graphite and the cathode is molten lead, which is tapped periodically from the cell. The chlorine is returned to the circuit.

When the mill solution has become saturated with soluble metallic chlorides, it is treated with metallic lead to precipitate the gold, silver, and copper; then with zinc to precipitate any lead that may have gone into solution, and then with zinc oxide (obtained by roasting high-grade ore) to precipitate all the iron, manganese, and other impurities. This leaves a commercially pure solution of zinc chloride. The precipitate is filtered off and the zinc chloride solution is evaporated to a 70 per cent solution if the product desired is zinc chloride, and to dryness, if the process is carried on to the production of metallic zinc and the recovery of the chlorine. If the product is sold as zinc chloride, the new chlorine supply must be generated by the electrolysis of salt solution. If the final product is metallic zinc, the anhydrous chloride is fused and electrolyzed by using molten zinc as a cathode and graphite as an anode. The zinc is tapped periodically and the chlorine returns to the circuit. The cells for the electrolysis of both lead and zinc are of the same pattern. They are made of concrete and lined with a special fire-clay tile. They have given entire satisfaction under continuous operation. The evaporation of the zinc chloride solution, which has always been troublesome not only from its corrosive qualities but from its tendency to form basic salts, is now conducted in a specially designed pan without difficulty from either of these sources.

The recovery of all metals by this process is said to average between 90 and 95 per cent. Based on the recovery of zinc alone, without taking into account the other metals recovered, the cost of operation is estimated at 2 cts. per pound of zinc, or 3¼ cts. per pound of zinc chloride produced. The higher cost of zinc chloride production is due to the fact that new chlorine has to be produced from salt and is not returned to the circuit, but, on the other hand, the chlorine in the zinc chloride sells at the same price as the zinc. The recovery of gold, silver, lead, and copper from the average complex ore more than covers the operating expense, leaving the zinc free from cost.

A pilot plant was constructed in Denver during 1924-1925 for the production of zinc chloride by this process. It is reported that this plant was operated continuously for several months with satisfactory metallurgical results but no market could be found in this territory for the zinc chloride and the caustic soda produced; also, that some difficulty was experienced in using the wet chlorine gas direct from the electrolytic cells. The company now proposes to install cells for the production of electrolytic zinc from the fused chloride and thereby return the dry chlorine gas to the circuit.

A plant, using chlorine gas for the treatment of lead-zinc ores, is reported to have been in commercial operation at Weston Point, England, in 1924.<sup>1</sup>

**Detinning Processes.**—These may be summed up in the Goldschmidt process,<sup>2</sup> although there are several modifications and patents that are closely related. They are all based on the fact that dry chlorine gas will attack tin, but will not attack iron to any appreciable extent. Therefore, if dry chlorine gas is carried over and through tin scrap, the chlorine and the tin combine with the evolution of considerable heat, forming tin tetrachloride, which is a heavy fuming liquid and drops off the scrap. The tin scrap must be absolutely dry and free from all organic substances, paper, lacquer, etc. It is not only necessary to remove all moisture, but all substances that can produce or attract moisture in order to prevent corrosion of the iron which would make it unmarketable. The tin scrap is compressed into bundles and placed into cylinders which are then closed. Chlorine gas is introduced at a pressure of several atmospheres. As the tin chloride is formed, the pressure drops. As soon as the pressure remains constant, the detinning is complete. Artificial cooling must be provided to prevent overheating.

The chlorine and the tin chloride are removed and the iron scrap bundles are carefully washed and sold to the open-hearth steel works. The tin tetrachloride is sold to the silk mills for weighting silk. In a modification<sup>3</sup> of this process the chlorine gas is dissolved in carbon tetrachloride and the tin scrap is placed in this solution, which also dissolves the tin tetrachloride as rapidly as it is formed and is thus withdrawn from the scrap. In another process<sup>4</sup> the scrap is heated with sand until the tin becomes brittle at temperature near the melting point. The mixture is then tumbled in a barrel until the tin is completely removed from the iron. The sand and the tin are screened from the scrap and are treated with dry chlorine gas in a closed vessel at a temperature that will volatilize and distil off the stannic chloride.

<sup>1</sup> POTTER, J. G., "Complex Lead-Zinc Ores to Be Treated by Chlorination and Electrolysis," *Eng. Min. Jn.-Press* (April 19, 1924), 646

<sup>2</sup> GOLDSCHMIDT, KARL, "The Detinning Industry," *Electrochem. Met. Ind.* (now *Chem. Met. Eng.*) 7 (Feb., 1909), 79-81

<sup>3</sup> U. S. patent 943986, MURRAY and FERNBERGER, 1909.

<sup>4</sup> U. S. patent 958877, C. J. REED, 1910.



**Aluminum Chloride Processes.**—Anhydrous aluminum chloride<sup>1</sup> possesses remarkable properties as a catalyst or reagent for the treatment of petroleum according to the Friedel & Crafts reaction: First, it converts all unsaturated compounds into saturated compounds by throwing out the excess of carbon in the unsaturated hydrocarbons. In this manner it converts unstable oils from asphalt-base petroleum into stable products of good odor and color similar to the paraffin-base petroleum.

Second, by simply boiling the heavier petroleum oils with anhydrous aluminum chloride at atmospheric pressure, these oils are cracked and 60 to 85 per cent of the heavy oil is converted into low-boiling fractions, leaving a residue of coke, or, if the distillation is stopped at the proper time, 60 per cent of the low-boiling fractions is produced, leaving 20 to 25 per cent of good lubricating stock.

Third, it completely desulphurizes the petroleum during refining.

The value of this reagent in the petroleum industry is so pronounced that over 700 patents have already been issued covering processes for its production, and practically all of the oil companies at one time or another have been engaged in research work relative to its commercial application.

Aluminum chloride is a white crystalline solid which volatilizes without fusing between 181 and 195°C. It is extremely hygroscopic and absorbs moisture from the air to form aluminum oxide and hydrochloric acid. This easy decomposition seriously interferes with its action as a catalyzer; it also produces transportation and storage problems on account of the difficulty of securing suitable moisture-proof containers.

The methods proposed for the manufacture of anhydrous aluminum chloride may be grouped under the following headings (reference to the technical paper quoted or to the original patents must be made for the details of these processes): (1) dry chlorine gas acting on aluminum metal; (2) dry hydrochloric acid gas acting on aluminum metal; (3) chlorine gas acting on mixtures of aluminiferous and carbonaceous materials; (4) chlorine gas or hydrogen chloride acting on aluminum carbide; (5) chlorine gas acting on aluminum nitride; (6) chlorine gas and carbon disulphide vapor acting on aluminiferous materials; (7) chlorine compounds of carbon acting on aluminiferous materials; (8) chlorine compounds of sulphur or arsenic acting on aluminiferous materials; (9) dry lead chloride reacting with aluminum metal or with aluminum carbide; (10) anhydrous calcium chloride reacting with aluminiferous materials; (11) aluminum chloride solutions prepared by any wet method, then evaporated and the crystals dehydrated.

All of these methods, with the exception of method (11), are performed at high temperatures, usually high enough to sublime any aluminum chloride formed. In fact, the great volatility of aluminum chloride is frequently the main inducement to reaction and many of the above processes are endothermic.

About 10 lb. of aluminum chloride are required to crack a barrel of oil containing 42 gal. It can be used several times before losing its catalytic activity. On a basis of 200,000,000 bbl. of petroleum refined annually, this industry alone would consume 800,000 tons of chlorine and 200,000 tons of aluminum or its equivalent in bauxite or aluminiferous material. There is not enough bauxite now available to meet this requirement, so every effort is made to utilize clay, feldspar, or other aluminiferous material as a source of aluminum. Chlorine is most cheaply produced by the electrolysis of salt, but to reach the limit of cost production for aluminum chloride some additional market must be found for the caustic soda produced as a by-product. For these reasons some form of volatilization process (see Chloride Volatilization Processes) may prove the more feasible for large-scale production.

In order to produce gasoline selling at 20 cts. per gal. aluminum chloride must be produced under 10 cts. per pound.

Aside from the above-mentioned data, there is very little information obtainable concerning this interesting problem of the production of cheap aluminum chloride and its utilization in the petroleum industry. Most of the research work, and particularly its practical application, is confined to the large oil companies and they publish nothing. It has been learned from other reliable sources that a satisfactory high-grade aluminum chloride is now produced from bituminous clays or shales and salt at a cost considerably below 10 cts. per pound, presumably by the chloride volatilization process, and that the small quantities of impurities such as  $\text{Fe}_2\text{Cl}_6$ ,  $\text{TiCl}_4$ ,  $\text{SiCl}_4$ , etc., do not interfere with the activity of the aluminum chloride itself; the only requisite is that it must be kept free from moisture. The problems of suitable equipment and satisfactory methods for producing, condensing, and handling the anhydrous salt have been solved.

The remaining problem is in the petroleum stills. The action of aluminum chloride on petroleum is not clearly understood, and there may be some chemical action as well as catalytic action. A change is noticed as soon as the salt is added to a heavy petroleum oil, and, as the critical temperature is approached, the reaction is very rapid. A large quantity of light oil is formed and carbon is deposited along with a thick, viscous residuum that is difficult to remove from the stills. The aluminum chloride is involved in this residuum and must be regenerated before it can be used again. The cracking of petroleum by this method is an intermittent and not a continuous process, as the published data would indicate, and it is a troublesome process to handle in the refining plants as now constructed. When all other phases of the process are solved commercially, refining plants will be constructed to meet the required conditions.

**Nickel and Cobalt Ore.**—Chlorine has been successfully applied to the recovery of nickel and cobalt from arsenical ores.<sup>1</sup> The Diehl process for treatment of nickel ores containing large amounts of magnesia and lime is interesting chemically, and suggestive of how basic ores may be leached. The ore, moistened with hydrochloric acid, is tube-milled at about 500°F. in an atmosphere of hydrochloric acid gas and then sent to a leaching tank with water. This water will take out practically nothing but a calcium-magnesium chloride solution, which is evaporated and treated with sulphuric acid to regenerate hydrochloric acid gas. The ore after leaching with water is leached again with hydrochloric acid, which then dissolves the nickel. This solution requires purifying and the apparatus is complicated, so the process has not yet been successful in competition with smelting.

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<sup>1</sup> BRALLIER, PAUL S., *op. cit.*, p. 849.



## CHAPTER XXXIV

### METALLURGY OF ZINC AND CADMIUM

By WALTER RENTON INGALLS, Sc. B., D. Eng.<sup>1</sup>

**Industrial Economics.**—Even before the World War began, the zinc industry of the world was experiencing radical changes. Looking backward, it can now be seen that 1896, when the Wilfley table was introduced, was an historic date in the metallurgy of zinc. An improved concentration of mixed ores requiring fine grinding was made possible and so the first step in the solution of the long-baffling mixed-ore problem had been taken. The smelters were, as a result, offered a new and bountiful supply of lead-bearing zinc ore, often high in iron, to which they had to adjust their metallurgy. Another important step in the separation of mixed ores occurred subsequently with the introduction of Wetherill's system of magnetic separation and Blake's system of electrostatic separation, but the climax occurred with the successful introduction of the flotation process at Broken Hill.

Finally, completing this historical summary, Broken Hill played a great part in the development of the electrolytic process of zinc extraction, which happened about 1916. In this connection it may well be mentioned that the first great commercial attempt in that direction was made by Ashcroft at Cockle Creek, near Broken Hill, in 1897. About twenty years later the immense plant at Risdon, in Tasmania, was put in operation for the electrolytic extraction of zinc from flotation concentrates from the same ore.

The original development of Broken Hill as a large producer of zinc ore had at least three great consequences: *viz*, it standardized smelting practice in Belgium and Germany; it compelled nearly all of the smelters of those countries to go on a zinc-lead basis; it showed that mixed ores could be profitably treated, and caused a search for them to be made in all parts of the world, which, within a few years, resulted in the development of such mines as the Butte & Superior, of Butte, Mont., the Bawdwin, of Burma, and the Riddersk, of Siberia, to mention only three of the first order.

The immense Australian ore supply was contracted to the three great German metal merchandising firms, which distributed the ore among the smelters of Germany and Belgium. Those smelters, coming thus into the possession of so large, so uniform, and so regular a supply of ore, the like of which in none of those respects had ever previously been experienced in the zinc industry, were able to standardize their smelting practice, not only as to a single works but also as to many works, which was metallurgically beneficial.

The Broken Hill zinc ore was rather high in lead. In previous times, zinc smelters generally were averse to smelting ore containing more than 2 or 3 per cent of lead, although a few smelters made a practice of treating ores relatively high in lead and recovering a considerable proportion of the lead therefrom. With the advent of the Broken Hill ore, the recovery of lead as a by-product in zinc smelting became the regular thing, and, in fact, the smelters of Belgium and Germany went practically upon a zinc-lead basis and even became insistent upon having a percentage of lead

<sup>1</sup> Consulting Engineer, 115 Broadway, New York, N. Y.

present in their ore that was far above what in earlier years had been regarded even as permissible.

Another radical change in the zinc industry, that was in progress previous to the war, involved the establishment of new loci of zinc smelting. The art of zinc smelting is one of a multiplicity of details in which the part played by many workmen spells the difference between success and failure. No matter how careful the plans of the engineer may be, they are likely to come to naught unless there be good workmen to carry them out; and the making of good workmen requires either long or intensive training. The possession of a class of workmen which has been engaged in zinc smelting during several generations is one reason why Belgium continued to be a great zinc-smelting country long after its own resources were exhausted. And because of the absence of such a class of smelters, it has been universally the experience until recently that the inauguration of new zinc-smelting enterprises in new regions has been attended by difficulties which generally have wrecked the adventurer.

While the experience has been along the above lines, it does not follow that the absence of trained workmen is prohibitive of the institution of zinc smelting. It has, indeed, been found possible to put a new plant in successful operation with "green hands," but this requires the presence of expert foremen for their instruction. It may even be found that it is possible to do better with a green crew correctly taught than with a personnel of the old type that has acquired by rule of thumb a variety of habits that are more or less bad. It is, indeed, not beyond the bounds of possibility that the operation of distilling zinc ore may be so standardized, regularized, and controlled that the present fallibility of the human factor will be eliminated to a large extent.

Germany, by virtue of its own great deposits of zinc ore in Upper Silesia and its contracts for the Broken Hill ore, was the great purveyor of spelter to the rest of Europe, especially to England. The first great consequences of the war were to suspend to a major extent the production of zinc ore in Australia, there being insufficient surplus smelting capacity outside of Germany and Belgium to receive it; and to throw a large part of the spelter requirements of Great Britain, France, and Russia upon the United States. The result of this movement was to raise the price for spelter to a figure not previously recorded in many years. Although this had a powerful commercial effect upon the American zinc industry, it did not have much influence upon the pyrometallurgy of this country. However, it had the immense effect of stimulating the process of electrolytic extraction.

Considering the art of zinc smelting upon its broadest lines, the variations between European and American practice are explained by variations in fundamental conditions, which may be summarized in the statement that in Europe labor is cheap and coal is dear; while in the United States coal is cheap and labor is dear. Thus, American smelters strive ever for mechanical substitutes for hand labor, and European smelters aim always to reduce coal consumption. There have been other determinative factors, the differences between which are, however, tending to disappear.

**Zinc Smelting in the United States.**—American zinc smelteries are of two kinds: *viz.*, those which use coal as fuel, and those which use natural gas. In Europe, coal is the only fuel, with the exception of one small plant which has furnaces designed for the use of producer gas or petroleum alternatively. American zinc smelteries are more standardized in their design than are the European, *i.e.*, the natural-gas plants are very much alike, while the coal-fired plants follow only two types. The varieties of roasting and distilling furnaces are but few. In European practice, on the other hand, there are many varieties of roasting and distilling furnaces, although, of course, they conform to standard principles.

The natural-gas smeltery of the United States is simpler, cruder, and far less expensive than the coal-fired plant. As it is built for the use of an ephemeral fuel, it is desirable, obviously, to keep the outlay of capital in such a smeltery at a minimum. For this reason the buildings and the machinery are of relatively light construction. Capital outlay is also saved because there need be no means for unloading, storing, and rehandling coal, no generators for gasifying it, and no regenerators for conserving it. Furthermore, the natural-gas plants are situated in regions where there is no market for sulphuric acid—therefore, there are required none of the adjuncts for acid manufacture.

The coal-fired plants of the United States, on the other hand, are, without exception, built in regions where there is market for sulphuric acid and are designed for acid manufacture. Economy in fuel is an essential consideration. Therefore, all of these plants are constructed with regenerative furnaces, or else are designed for heat recuperation in the form of steam. These plants are built substantially, with a view to long life, and are relatively costly. The old, direct-fired Belgian furnaces that were first introduced in zinc smelting in the United States no longer are in use, but examples of them are still to be found in abandoned plants.

The American zinc plant is usually a perfectly integrated affair. Blende is taken in and roasted, and spelter and sulphuric acid are produced. In a few instances a rolling mill forms a part of the plant and spelter is manufactured into sheet. The ore supply of American smelters is mainly blende. The quantity of calamine received by them is insignificant. European smelters, on the other hand, still get a great deal of calamine. Their supply of blende, arriving largely by sea, is frequently received first at a roasting plant, where it is desulphurized and sulphuric acid is made. The roasted ore is then reshipped to the smeltery or distillery. At the latter, roasting furnaces are absent. To a small extent roasting and distilling are done as different operations, in different plants, in the United States, but not so much so as in western Europe. The zinc smelteries of Silesia are fully integrated affairs like the ordinary American plants.

Another essential difference in the designs of American and European zinc plants relates to means for the further treatment of the residues from distillation. European smelters treat more leady ores. They conduct their distillation at a higher temperature than in American practice. Their retort residues are, therefore, relatively low in zinc, but high in lead. They are delivered to a washery, where a lead concentrate is produced by jugging and tabling, which is sold to lead smelters. In American practice residues that are sufficiently high in lead and silver are shipped directly to silver-lead smelters. If low in silver and lead but high in zinc, which is usually the experience, the residues are passed on for the extraction of their remaining zinc as oxide, which is accomplished by burning in furnaces of the western Wetherill type. In one or two instances, however, the residues are subjected to mechanical concentration and the concentrates are re-roasted and redistilled.

It will be perceived, of course, that the difference in the designs of the two main types of American zinc smelteries, and the difference between them and European plants, are determined mainly by economic conditions. The American zinc smelter translated to Europe would do the same things as his European colleagues, and *vice versa* would the European if brought to America. Both of them speak the same language, metallurgically, and are well informed respecting mutual practice. The differences in the practice of the art which result from differences in conditions will be discussed more fully in subsequent pages.

Further comparisons between European and American practice may be most clearly indicated by sketching the principal parts of a modern zinc-smelting works. All of what follows in this chapter pertains to the smelting with coal-fired furnaces.

only and does not include the smelting with natural gas in the United States—which is on the wane. Nor are the figures given intended to represent the practice with Silesian furnaces.

The ore is delivered into the works in railway cars, from which it is unloaded directly into the storage bins. The means for unloading, sampling, storing, and reclaiming have, heretofore, been rather crude in many of the American works, but recently there has been an increasing tendency to adopt the superior methods that have long obtained among lead and copper smelters.

The ores coming to the zinc smelter are classified as calamine and blende. In Europe, the former is still calcined. In America, the calcination of calamine was abandoned by the smelters many years ago, the advantages being pronounced unequal to the cost. Blende, of course, must always be roasted.

The roasted ore goes to the mixer, where it is united with the proper proportion of reduction coal. Mechanical mixing and careful attention to this important part of the process were early practiced at La Salle, but at other plants in the United States the methods were far below European standards until recently.

Following European practice, American distillation furnaces are now commonly built entirely above the ground, the unclean, uncomfortable, and unsanitary subterranean galleries of old being abolished. The Europeans are still ahead, however, in ventilation of the furnace houses. They generally lay out their furnaces in line, while in this country they are laid out in rows.

Metallurgically, the essence of zinc smelting is the temperature of distillation. Speaking generally, the higher the temperature the better is the extraction of zinc. But with bad ores, and bad practice, high temperature is not feasible, for the furnaces and retorts will not stand it. A bad ore may be smelted with but little trouble, at a relatively low temperature, but the extraction of zinc will be poor. The aim of the zinc smelter is to smelt a bad ore if he has to and to obtain the maximum possible percentage of zinc from it.

In general, the Europeans excel the Americans in this respect. They mix their ores more scientifically, they make better retorts, and they build stronger furnaces—all of which contribute to an ability to drive their furnaces at higher temperature than Americans have yet attained—and at the same time they utilize ores that are rather high in lead. In so smelting, they make a leady spelter, but a simple refining in a reverberatory furnace removes the excess lead. In only one American works has that been practiced.

European smelters also generally recover blue powder as a commercial product. This is obtained from the prolongs, which condense a proportion of zinc that would otherwise be lost. American smelters do not use prolongs. Although in trials of them, an additional 1 or 2 per cent of the zinc has been obtained, they have found it to be unprofitable—this again reflecting the difference in labor conditions.

The previously mentioned main differences between European and American practice in zinc smelting are explained by the reasons previously mentioned. Per ton of raw sulphide ore, the American smelter uses about  $1\frac{3}{4}$  to  $2\frac{1}{4}$  tons of coal and 2 to  $2\frac{1}{2}$  man-days of labor; and extracts about 84 to 88 per cent of the zinc that is in his ore; if he treats lead-bearing ore, he may recover 50 to 60 per cent of the lead.

The European smelter uses about  $1\frac{1}{4}$  to  $1\frac{3}{4}$  tons of coal and extracts 88 to 90 per cent of the zinc that is in his ore, and about 50 to 70 per cent of the lead.

Properly, such figures as the above should be accompanied by qualifications and explanations that would run to pages in length and would constitute an elaborate treatise upon the metallurgy of zinc. Therefore it should be remembered that the figures are used merely as broad generalizations for the purpose of exhibiting, in tabloid form, the lessons deduced from the differences in the art as practiced in Germany and the Low Countries and in the United States. They mean that the

Europeans, with the aid of better furnaces and superior technical direction, are able to smelt more refractory ore than are Americans, and yet extract a higher proportion of the valuable metals. They have built more substantial plants—secure from fear of geographical migration of their industry—for the sake of increased durability and maximum economy of fuel.

**General Principles of Zinc Smelting.**—The metallurgy of zinc divides itself into two main branches: *viz.*, pyrometallurgical, and hydrometallurgical. Under the latter head fall the chemical and electrolytic processes, according to whether chemical reagents or electric current be the agent for precipitating zinc from its solutions. Under the former head come the processes that are commonly generalized as zinc smelting, but the latter word is more or less a misnomer, inasmuch as there is commonly no such thing in the pyrometallurgy of zinc as smelting. In all processes, zinc oxide is directly reduced by carbon, volatilized and distilled, and the only association with smelting as commonly understood is that the metal, if that be the end product, is obtained in a molten state.

The zinc pyrometallurgical processes are, therefore, all processes of distillation. They may be subdivided into: (1) simple distillation for spelter; (2) distillation for zinc and lead, which may be called zinc-lead smelting with a nearer approximation to the idea of smelting than anything else in this metallurgy; and (3) distillation for zinc oxide or zinc-lead oxide, in which the zinc following reduction is burned immediately and collected as oxide instead of being condensed as spelter. These three branches of zinc pyrometallurgy may be, and are, combined in a variety of ways. Although the term "zinc smelting" is not precise, as has hereinbefore been pointed out, it will be employed freely, for it is in common usage and everyone knows what is meant by it.

The art of zinc smelting is simple in principle, but complicated in practice. It depends upon the reducibility of zinc oxide by carbon, or carbon monoxide, or both. Consequently, zinc sulphide—blende—must first be roasted to obtain the oxide. Zinc silicate ( $\text{ZnO} \cdot \text{SiO}_2$ ) and zinc ferrite ( $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$ ), which may be formed during the roasting, are both reducible directly by carbon.

Zinc oxide begins to be reduced by carbon at temperatures ranging from 900 to 980°C., about 940° being a figure that has been determined for roasted Joplin blende. The result, however, is affected by the percentage of carbon dioxide present in the gas. According to Bodländer, zinc oxide reduced at 1125°C. is reoxidized by carbon dioxide if the latter be present in more than 0.2 per cent of the volume of the gas. With increase of temperature the permissible percentage of carbon dioxide increases also, until at 1500°C. there may be 0.76 per cent.<sup>1</sup> Dr. C. H. Fulton in a recent paper<sup>2</sup> gives somewhat different ideas. He says that carbon dioxide under 1 per cent has no effect upon zinc vapor either above or within the condensation temperature range, but within that range, 500 to 700°C., distillation gases must not contain more than 2.5 per cent carbon dioxide if oxidation of the zinc is to be avoided entirely; when present between 2.5 and 5 per cent, the action of carbon dioxide is comparatively slight; when more than 5 per cent is present, oxidation is pronounced, and blue powder begins to form.

Without being precise as to the limits, the effect of carbon dioxide in the retort gas is of supreme importance in the metallurgy of zinc. It explains why metallic zinc may not be distilled in a blast furnace and why the product is blue powder in one—

<sup>1</sup> Z. Elektrochem., 8, xlv, 833–842.

<sup>2</sup> Trans. A. I. M. M. E., 60, 280–302.



stage smelting in the electric furnace Zinc oxide can be reduced in the blast furnace just as it is in the Wetherill furnace—which is a species of blast furnace—but in the Wetherill the reduced zinc is then intentionally burned to oxide By limiting the presence of carbon dioxide, combustion of the zinc may be avoided, but the oxidation that results in blue powder cannot be avoided This is why the reduction-distillation of zinc is limited to relatively small retorts, in which the necessary and peculiar conditions can be maintained, and why the process must be so arranged as to be divisible into stages Even so, although it is possible to establish the condition of very low carbon dioxide in the gas issuing from the retort during the period of active distillation, it is seldom possible, perhaps never, to attain the minimum theoretically required, and there is always also a certain production of blue powder by physical conditions, especially sudden chilling of the zinc vapor, which causes the metal to drop down in solid form instead of liquid, with the analogy of the condensation of aqueous vapor as snow or hail instead of rain

Looking into the condenser in place in the furnace in operation, the zinc vapor may be seen emerging from the retort as a fog, assuming a swirling motion counterclockwise and wreathing spirally around the interior surface of the condenser Cooling in contact with that surface, the droplets run down the sides, and fall from the top, collecting in the pool in the bottom When they have experienced superficial oxidation they fail to coalesce, but the latter action may be brought about to a certain extent by pressure, or, much better, by a rubbing that removes the superficial coating of zinc oxide The zinc vapor that escapes from the condenser into the prolong is precipitated in the latter as powder as a consequence of the sudden chilling therein, although the powder is but relatively little oxidized For this reason, the blue powder from the prolong is much higher in zinc than the blue powder from the condenser, and when it is collected as a marketable product the prolong dust rather than the condenser dust is always sought

As practically conducted, zinc distillation is an intermittent process, divided into four stages, *viz* (1) The maneuver, during which the spent residues from the previous charge are withdrawn broken retorts are replaced, all retorts are recharged, etc This stage requires 3 to 5 hr (2) Preliminary reduction, during which water is expelled, hydrocarbons are driven off, and the oxides of metals other than zinc, such as iron and lead, are reduced During this stage, which occupies 2 to 3 hr, the temperature of the retorts is raised gradually The issuing gas is first pure coal gas and burns with a luminous flame at the noses of the condensers This flame becomes less bright as the reduction of the metallic oxides begins and the percentage of carbon monoxide increases, and gradually becomes purple When the flame becomes tinged with bluish green the beginning of zinc distillation is indicated This marks the end of the second stage of the process, although the dividing line is not sharply drawn When zinc begins to distil and condense the percentage of carbon dioxide in the gas is still high, and consequently there is much formation of blue powder at this time (3) Active distillation during which the zinc is reduced and distilled rapidly, this period running about 13 hr (4) Waning distillation in a period of about  $4\frac{1}{2}$  hr, during which the last part of the zinc is expelled the average rate of hourly condensation during this period being only about one-half that of the previous period A high temperature is maintained during this period and the resistance of the retorts, relieved of the endothermic reaction within them, is tested most severely Finally, all of the zinc is expelled that can be at the temperature used, the condenser flames become purple again, the cycle has been completed, and preparations are made for the maneuver of the next day

The foregoing indicates one condition which stands in the way of making zinc reduction distillation a continuous process, *viz*, the necessity for performing the second stage separate from the third In practice, this is done as one of the steps in a

24-hr cycle in the distilling furnace, but it may be done in a separate furnace as a separate act and then zinc distillation may be conducted continuously. This has been proved by electric furnaces operated on preheated, or prereduced, charges. The same idea of prereduced charges has been actually, though not generally, used in practical pyrometallurgy, not to the extent of enabling continuous distillation, but enough to relieve the retorts of some of their work and extend the time available for active zinc distillation.

Another important condition stands in the way of continuous distillation, however, though it is not insuperable, *viz* intimate contact of zinc ore and carbon is necessary, which implies fineness of grains. Indeed, zinc ore, being so largely the product of concentrating mills, including the excessively fine flotation slimes, comes to the distiller fine anyway. Now, when a retort is charged with fine ore a rod must be run through the top (this is called "spiecing") in order to afford a channel for egress of the gas and vapor during the early stage of distillation. However, the gas and vapor must seep up through the charge itself in order to get into the channel. Under certain conditions, *e g*, too great depth, excessive fineness, etc., it may be unable to do that easily. The result then may be the accumulation of such internal pressure that the entire charge will be blown out of the retort. This is why the distillation of ore ordinarily fine is practically limited to the depth that it has in the Rhenish retort, *i e*, about 12 in. For the distillation of coarser charges in Upper Silesia, deeper muffles were formerly used, but when they began to treat richer and finer ores the Silesian distillers had to adopt the Rhenish retort.

The same condition applies to vertical retorts designed for continuous operation, although the earlier designers did not think of it. The gas and vapor could not get out. One or more inventors thought subsequently to meet this condition by arranging a row of outlets down the shaft. It is possible, also, that the condition may be met in other ways. In the Roitzheim-Remy furnace that has been introduced in Germany this problem appears to have been mastered, but this furnace has so far been used only for distilling secondary products.

It will help in the consideration of the whole subject of zinc pyrometallurgy if these fundamental principles of practice are fixed well in mind. There is another principle, namely, the matter of temperature of distillation, on which depends largely the extraction of the zinc, the quality of the primary product, and the cost of the process.

Although zinc oxide begins to reduce, under certain conditions, at about 940°C, the speed of the reaction is greatly increased by elevation of temperature, and, since it is for technical considerations important in practice to complete the working of a charge in 24 hr, it is essential in practical smelting to conduct the operation at a considerably higher temperature. Given a certain time for the distillation, which is commonly about 17 to 18 hr, the remaining 6 to 7 hr being occupied in discharging and recharging the retorts and expelling the hydrocarbons, the higher the temperature, the more complete will be the extraction of the zinc. But here enter other complications. The silicofluorides of iron, lime, etc. begin to form at about 1200°C, and as the temperature rises further more infusible slags can form, and the gangue of the ore containing these elements may give rise to slags which quickly corrode and destroy the retorts in which the distillation of the zinc is being conducted to such an extent, indeed, as to make the process impracticable. Moreover with increase of temperature other metals, especially lead, distil over with the zinc, necessitating a further refining of the latter in order to produce a marketable quality of metal. An ordinary temperature of distillation is 1250 to 1350°C. The performance of the process at 1200°C is known as "slow driving," while 1400 to 1450°C is "hard driving." These temperatures are maxima and are as registered inside the retort. The temperature in the laboratory of the furnace, *i e*, outside the retorts, is about 100° higher at the time when the maximum is attained.

American smelters lean to slow driving while Europeans adhere to hard driving. In either way there is some variation in the management of the furnace. Having arrived at the third stage of the process one smelter may raise the temperature quickly and maintain a high temperature right through the third and fourth stages, while another may raise it more gradually and attain a maximum during the fourth stage when he is "pinching" the charge. As already pointed out, with increase of temperature other metals, especially lead, distil over with the zinc. Given the lead contents of charge and spelter, an experienced metallurgist can tell pretty nearly what was the temperature of distillation. American smelters make a practice of keeping separate their first draw of metal, which will be higher in cadmium and lower in lead than the second draw. The last draw, which may be the third or fourth, will be highest in lead. European smelters, distilling uniformly at high temperature, are apt to make a leady spelter, which has to be refined by melting in a reverberatory furnace and allowing the excess of lead to separate by gravity. This has the incidental advantage of equalizing the spelter and producing slabs of uniform composition. Spelter molded directly from the drawing kettles is apt to be irregular in composition and there is more or less complaint against American brands on this account.

The matter of temperature introduces consideration of the behavior of the gangue of the ore, for the higher the temperature the more dangerous become the slags. The historic method of taking care of the slag is to have present a great excess of reduction material to absorb and hold it like a sponge, but in modern practice care is taken not to permit the formation of anything like an easily fusible singulosilicate, but so to compound the charge that the slag will be a bisilicate or trisilicate. The retorts must be as strong, dense, and non-corrodible as it is possible to make them, and the lining of the furnace—in fact, the general structure, and especially the middle wall, or middle ledges—must be of the maximum durability. The successful withstanding of a temperature of 1550°C for a campaign of upward of three years requires refractory material, masons' work, and general furnace design of a high order of excellence.

Complying with these conditions, good practice tends strongly to hard driving, for the extraction of zinc is greatly increased without a corresponding increase in the consumption of coal as compared with slow driving. The European smelters were hard drivers, even in prewar times, while the American are generally slow drivers. Note must here be made that a furnace designed for the distillation of a certain ore at a relatively low temperature cannot necessarily be speeded up by simply raising the temperature. In so doing the capacity of the condensers might be overtaxed and zinc distilled too rapidly might be forced to burn uncondensed at their noses. Reference may here be made again to the subject of prolongs, sheet-iron extensions of the condensers. European distillers use them generally, American but rarely. They save considerable zinc escaping from the condensers, but in American practice this is deemed insufficient to compensate for the extra labor of taking them down and putting them up at each draw. With the Rhenish and Silesian furnaces drawing is less frequent, nor do the prolongs have necessarily to be taken down during drawing.

In the distillation of zinc ore only a part of the zinc is obtained directly as spelter, the proportion commonly ranging from 60 to 70 per cent. The remainder goes into between-products, from which it is recovered by redistillation, or is lost. The between-products are the withdrawals from the front ends of the retorts (called "samples"), ladle skimmings, condenser cleanings, condenser concentrates, and floor sweepings, the last taking in the old luting of the condensers, metal splashes, etc. In American practice these between-products, which may aggregate 20 to 30 per cent of the weight of the ore charged, are lumped together as "blue powder." Properly speaking, the blue powder is the metallic dust that is collected in the prolongs, if they be used, or is pulled out of the condensers along with the spelter to be subsequently segregated as ladle skimmings.

The blue powder collected in prolongs may be sold, after sifting, as a commercial product, but, in general, all of the between-products are redistilled. This is done either in a separate furnace devoted to that purpose, in European practice; or in the ore-distilling furnace, in American practice. In the latter a certain number of retorts in the cooler part of the furnace are appropriated for this. In the Hegeler furnace these are the retorts near the chimney end; in the Siemens furnace, the upper two rows. With the Hegeler furnace the blue powder is usually distilled alone; with the Siemens furnace a proportion of fresh ore is usually mixed with it.

The proportion of blue powder is widely variable and to a considerable extent is within the control of the metallurgist. Thus, one may draw a large sample from the retorts, while another may take but a small one. A third may be indifferent respecting his residues, intending to burn them subsequently on grates. Thus, the matter of between-products correlates to a greater or less extent with the percentage of ultimate metal extraction. It will be observed, of course, that all of the material that is subjected to redistillation is bound to experience a secondary loss of zinc. It may be remarked further that the consumption of coal, labor, etc., is commonly calculated upon the basis of fresh ore charged. Thus, if it is said that 1 ton of coal is used for the distillation of 1 ton of ore, that quantity of ore plus about 0.3 ton of between-products is meant.

The losses in zinc distillation may be generalized as being due to failure to reduce and failure to condense. The latter may be subdivided into losses by escape and losses by absorption. The loss by failure to reduce exhibits itself in the retention of zinc in the residues in the retorts. This is always the largest single item of loss. It is especially ascribable to zinc being held back by sulphur, which may be due not to poor roasting but to the presence of sulphates in the ore which liberate their sulphur during the reactions in the retort. Absorption losses occur in the clay of the retorts and condensers. With the former the zinc forms a spinel, from which it is non-recoverable, but from the condensers a considerable portion of the absorbed zinc may be regained by crushing and concentrating mechanically. Losses by escape occur through the breakage of retorts, the filtration of zinc vapor through them, the flight of uncondensed zinc from the noses of the condensers, and from the burning of the residual zinc vapor in the retorts when the condensers are taken down at the end of the daily cycle. The flight of zinc from the condensers, which usually amounts to 1 or 2 per cent, may be prevented by the use of prolongs, but inasmuch as they have to be removed at each drawing of metal, that does not pay with American labor conditions and the practice of making three or four draws per day. With European conditions and the Rhenish practice of only one draw per day things are quite different.

In good practice, both in Europe and America, the extraction of zinc in distillation runs from 86 to 90 per cent of the original content of the ore. An analysis and explanation of the differences and the determining factors would necessarily be lengthy and complicated. Perhaps no other branch of metallurgy is so involved. Before the ore reaches the distilling furnaces it has been subject to the losses of roasting and handling. These may aggregate 3 per cent. On the basis of raw blende, therefore, the plant extraction will be about 83 to 87 per cent against the 86 to 90 per cent of the distilling division. There are, however, many works that do not do so well as the lower figure.

This statement of general principles outlines the complexity of the art of zinc distilling in arriving at the most economical balance among many conflicting conditions. Within the present limits of space it is impossible even to hint at many details of the

art. The manufacture of retorts and condensers, the design of distilling furnaces, the organization of labor for their operation, the matter of density of charge—these and many other things are subjects for voluminous analysis and discussion. Bulky treatises are devoted to them without exhausting the subject.<sup>1</sup>

**Blende Roasting.**—In the metallurgy of zinc, blende roasting is performed under two major heads, which may be described as dead roasting and partial roasting. In the former process the objective is to eliminate all of the sulphur that it is possible to do economically. This is essential as a preliminary to reduction and distillation for spelter, or for reduction and burning for oxide. In connection with either of those purposes retention of sulphur, especially as undecomposed sulphide, means loss of zinc in substantially the proportion that it is bound with the sulphur. In roasting blende as a preliminary to reduction and distillation in an electric furnace a partial desulphurization is all that is needful if the furnace is to be operated on the principle of gangue scorification, in which event the presence of some sulphur is desirable for matte-forming purposes. Thus, in the Scandinavian electrothermic metallurgy from 2 to 4 per cent of sulphur is left in the roasted ore.

As a preliminary to electrolytic zinc extraction also the roasting is only partial, but in this instance it is desirable to have the maximum oxidation of zinc sulphide and a certain production of zinc sulphate. The sulphate passes subsequently into solution, and by the following electrolysis sulphuric acid is formed, replenishing that which is otherwise lost in the process. Indeed, there is a tendency toward the accumulation of surplus acid unless the roasting be carefully controlled. The latter is done by roasting at a relatively low temperature, about 700°C., and regulating the volume of excess air. It is possible to conduct the process of partial roasting so as to convert nearly all of the zinc sulphide into zinc sulphate, as is done in the Coolbaugh process; or the roasting may be done in two stages, as at Risdon in Tasmania, where the first is designed to give a rich gas, suitable for sulphuric acid manufacture; and the second is adjusted to complete the decomposition of the zinc sulphide and produce the zinc sulphate necessary for the electrolytic process. By the two-stage method, which is performed with the aid of two furnaces, the surplus sulphur is used commercially and the acid balance in the electrolytic process is easily controlled.

In the dead-roasting of blende the furnace temperature attains about 900°C. at the maximum. In properly conducted operations blende containing 30 per cent sulphur is burned down to 1 per cent of sulphur, or less, reckoning as "sulphide sulphur" so-called. Roasted ores containing lime may show low sulphide sulphur and high total sulphur, owing to the formation of calcium sulphate. The dead roasting of blende may be done either with a view to utilizing the sulphur dioxide for acid manufacture or to the wasting of it through chimneys. For the former purpose, muffle furnaces are necessarily employed, for the latter, reverberatories or any type wherein the flames pass directly over ore on the hearth.

Blende roasts best when it is crushed to about the size of wheat grains, or 1- to 2-mm. diameter, or, say, to pass a 6-mesh screen. The roasting of excessively fine ore, such as flotation concentrates, is more difficult, owing to its greater volume and the inability of the air to obtain free access to the particles except when they are exposed on the surface of the bed. There is, naturally, more dusting from stirring and from dropping from hearth to hearth with fine ore than with that which is more

<sup>1</sup> The reader is referred to INGALLS, "Metallurgy of Zinc and Cadmium," LODIN, "Metallurgie du Zinc," LIEBIG, "Zink und Cadmium," HOFMAN, "Metallurgy of Zinc and Cadmium," and PROST, "Cours de Metallurgie des Metaux autres que le Fer."

coarsely granular. The collected flue dust may be as high as 5 per cent of the weight of the ore charged into the furnace.

Theoretically, blende should burn autogenously, *i.e.*, without the use of extraneous fuel. Commonly, however, a widely varying percentage of coal is burned in the fire box. This may be as high as 50 per cent with a poor type of furnace and as low as 10 per cent with a good type. The difference is attributable to variation in the conservation of heat within the furnace and the control of air supply, avoiding any large excess which must be uselessly heated. Practical trials have lately been made with the Ord furnace at Cuba City, Wis., and Columbus, Ohio, which is designed to dead-roast blende autogenously, and there is prospect that this will be successfully accomplished in conformity with theory and in one furnace. It has been known, of course, that blende might be self-roasted down to 8 or 9 per cent sulphur in one furnace and then finished by means of a Dwight-Lloyd sinterer.

Many types of blende-roasting furnaces have been designed and used. These are described in the metallurgical treatises to which the reader has been referred. Some of these furnaces remain in use, especially in Europe, as relics of old-time practice, but in the United States relatively few forms of furnace survive. If sulphuric acid is to be made, requiring a muffle furnace, all American smelters use the Hegeler, except one which employs a modified Spirlet and one which has adopted the Ord furnace. If sulphuric acid is not to be made, the furnaces that are in use comprise the Ropp, the Zellweger, the Rissmann-Ruebel, and the Brown (both horseshoe and straightway). In Europe, practically all of the blende-roasting furnaces are muffled. The Rhenania furnace is still extensively employed, but the present favorite among hand-raked furnaces is the Delplace. As a mechanical furnace, the Spirlet has found favor with a good many European smelters.

No great amount of space need be given to the description of the reverberatory roasting furnaces. At the present time none but those which are mechanically raked would be used, and they would be used only in regions where there is no extensive market for sulphuric acid and where there is freedom to disperse the sulphur gases into the atmosphere. The smelters west of the Mississippi River in the United States, which use natural gas as fuel, encounter such conditions and consequently employ mechanical reverberatory furnaces. This type might also be employed in some remote places, *e.g.*, in Siberia, but in general, it may be considered that its day has gone.

The mechanical reverberatories differ mainly in their stirring mechanism, which must be designed so as to have some protection from the heat of the furnace—especially its working parts. In the Brown furnace the rabblers are carried by wheels running on rails in recesses at the sides of the hearth, the stirring arm, or beam, traveling through slots, which are arranged in the masonry of the furnace. This furnace may be built with the hearth in annular form or in straight line, the principle of the design being the same either way. The Ropp furnace is similar in general principle, but the carriage itself runs on a track in a tunnel under the hearth, while a standard projects upward through a longitudinal slot in the center of the hearth and carries the rabble over the latter. The Ropp furnace is built only as a straight-line furnace. The Cappeau furnace is the same as the Ropp, but the hearth is supported on legs, so that the stirring carriage beneath it runs in the open instead of through a tunnel. The Zellweger furnace has two deep troughs on each side of the hearth, wherein are laid the rails for the wheels of the stirrer. The stirrer itself straddles the hearth like the axle of a wagon. The stirrer rotating over the hearth in its forward motion has a very good action upon the bed of ore, but, unfortunately, the wheels that carry it are necessarily of large diameter, thus entailing a high roof. The volume of the reverberatory chamber is, consequently, so great that the furnace proved very wasteful of fuel. The Rissmann-Ruebel furnace was designed to correct that drawback. Two hearths were built side by side and the wheels were caused to run on a track between

them, the axle of the pair projecting right and left through slots in the opposite sides of the pair of furnaces and thus carrying the rotating stirrer over the respective hearths. These several furnaces have been described in great detail in the metallurgical treatises of Ingalls and Hofman.

The mechanically raked reverberatories are relatively cheap in first cost. They are also relatively cheap in operation, although their fuel consumption is commonly high, owing to the inability to control closely the volume of air passing through them and the common use of an exaggerated excess. This is reflected in the gases passing to the chimney, which seldom contain more than 2 per cent of sulphur dioxide by volume, whereas the gases from muffle furnaces are seldom lower than 5 per cent, and commonly are 6 or 7 per cent. Of course, this is not a strictly correct comparison, for in speaking of the muffle furnaces no account is taken of the gases from fuel consumption. However, it affords a rough idea. Within these limitations the mechanical reverberatory is a good desulphurizer, and with it no difficulty is experienced in dead roasting favorable blende down to a sulphur content of less than 1 per cent.

In roasting blende with a view to using the sulphur gas, a muffle furnace is requisite, of course. For this purpose American zinc smelters use only the Hegeler, with but one or two exceptions. The Hegeler furnace has undergone but little modification since its introduction at La Salle in 1882. It is built in the form of a double series of hearths, right and left, seven high. It is always fired with producer gas. Flues for the combustion of the gas pass under the lower hearths, the heat of the burning sulphur being self-sufficient in the upper hearths. The raking operation is intermittent and only semimechanical. At each end of the furnace there is a structure with platforms corresponding with the hearths, on which the rabblers are supported when not in action. A manipulating crew of men is required at each end of the furnace. A more or less complicated mechanism causes a rod to be thrust through the hearth to be rabbled. The operator at the other end of the furnace attaches the rabble to the end of the rod, which is then drawn back through the hearth. When the rabbling of one side of the furnace has been completed, the structure supporting the rabblers is swung around, after which the rabblers are drawn through the other side of the furnace in the opposite direction. There are ports in the sides of the furnace which may be opened for the barring up of hearth accretions. In the roasting of certain sorts of ore, especially leady ore, this is a tedious and vexatious obligation.

The improvements in the Hegeler furnace since its original introduction have increased its dimensions, bettered its construction with respect to masonry and iron work, and improved the mechanism for operating the rake rods. Whereas two men were formerly required per shift at each end, many furnaces are now so arranged that one man per shift can do the work. In spite of these improvements, however, the Hegeler furnace remains a clumsy means for blende roasting. It effects good desulphurization but yields only a moderately strong gas for acid manufacture. Operating cost is relatively high, and the cost of installation is huge. The use of the Hegeler furnace under European conditions would be practically out of the question.

Owing to the relative cheapness of labor abroad, European metallurgists never had the same incentive as Americans to go in for mechanical roasters. They have devised several types, but none has come into general use and but few have even survived. The latest and most promising design was the Spirlet. This is a circular furnace, about 14 ft. in diameter outside, with four superimposed hearths. Two of the hearths are stationary and two of them are rotated by external mechanism. The hearths are built of special tile, inside of a steel ring, in such a way that alternate tiles project downward to serve as rabblers for raking the ore on the next hearth below. The space between the hearths is small, being only 6 $\frac{3}{4}$  in. in height. Only the lowest hearth is heated externally. The air for roasting and for combustion in the fire boxes is preheated. Both the stationary and moving hearths have lateral seals working in

annular troughs. When it is necessary to repair the hearths they are lifted out bodily, one after another, by means of a crane.

The Spirlet furnace is thermally well designed. As there is no interior mechanism and the hearth chambers are small, close control of the air is possible. The roasting gas commonly contains  $7\frac{1}{2}$  per cent sulphur dioxide and may be run up to 10 per cent. Coal consumption is low, even as little as 7 or 8 per cent, and the requirements of labor and power are small. The furnace is capable of installation in a battery of relatively small units (the standard furnace burning about 10,000 lb. of blende per 24 hr.), an arrangement which the sulphuric acid maker likes for the sake of regularity of the gas delivered to him. The maintenance of the rabblies is rather troublesome, however, and there are mechanical difficulties with respect to the general design and operation of the furnace. Some of the Belgian smelters have made them work, apparently with satisfaction. Extensive installations of them were made in three American plants. At two of these a great deal of trouble was experienced and the Spirlet furnaces have been practically abandoned at them. At Argentine, Kan., the metallurgists retained them and, after redesigning them, producing what may be called the American Spirlet, found them quite satisfactory. An extensive installation of Spirlet furnaces was made at Broken Hill, New South Wales, and proved satisfactory there. These experiences indicate that, while the Spirlet is theoretically a good furnace and may be made to work well, a great deal of care in introducing it must always be exercised.

Notwithstanding the economic upheaval of the war, substantially the same conditions as formerly continue to prevail among European zinc smelters, and at present they show a strong tendency to revert to hand-raked, muffled furnaces, archaic as the thought at first sight may appear to be. For a good many years the standard furnace of this type in Europe was the Rhenania. This is a double furnace with long hearths, three high, the ore traveling them successively. In its latest development the flame flues passed under the lowest hearths and then over the highest, the heat of the burning sulphur itself being sufficient for the middle hearth. There was nothing especially novel in this type of furnace. Its distinguishing characteristics were the excellence of its masonry (it being built of carefully fitted tiling), the small height of its roasting chambers, and the smallness of its working doors, all of which promoted the exclusion of unnecessary air. Nevertheless, the consumption of fuel was higher than was desired and the work of rabbling and moving forward the ore was hard. Therefore this furnace was abandoned in several of the plants in Belgium and the Delplace was substituted.

The Delplace furnace is simply a modern development of the old Maletta shelf burner, with the difference that the lowest shelf is muffled and the air for roasting is preheated. The fire boxes are designed in the nature of gas producers. The heating of this furnace may be described as being by semigas firing. The furnace is built in blocks of six or more units, which, of course, promotes heat conservation. The furnace unit is seven shelves, which are raked from the front. The shelves are about  $4\frac{1}{2}$  ft. wide and about 6 ft. long. The blende in its downward course travels a distance of about 41 ft. The roasting chambers are low, being about only  $6\frac{1}{2}$  in. high. The unit of a battery roasts about 2,200 lb. of blende per 24 hr.

The first cost of the Delplace furnace is relatively low, but the labor for operation is relatively high. The design of the furnace from the thermal standpoint is excellent. Built in blocks, as it is, radiation is reduced to the minimum. With the small roasting chambers and few openings into them the admission of unnecessary air is also restricted. The air for blende oxidation is preheated by the waste gases on their way to the chimney. With these favorable conditions blende is roasted in the Delplace furnace with the use of only 10 per cent fuel, while the roasting gases leave the furnace with a content of  $6\frac{1}{2}$  to 7 per cent sulphur dioxide.



With a furnace designed to keep the loss of heat by radiation at the minimum, to keep the use of excess air at the minimum, and to transfer the surplus heat from the combustion of sulphur from parts of the furnace where it is not needed to other parts where it is, blende should be roasted without the use of any extraneous fuel. It has been aimed to accomplish this by means of the Ord furnace, which is a muffled form of the well-known Wedge furnace, with certain modifications, the latter being especially in the way of by-passing portions of the ore so as to equalize the sulphur combustion throughout the furnace. The Ord furnace received a preliminary trial at Cuba City, Wis., and was subsequently built for regular operation at the works of the American Zinc, Lead & Smelting Co. at Columbus, Ohio. So far the prospects for accomplishing the purpose look favorable, but, of course, this furnace has not yet passed the test of working satisfactorily over a long time.

The development of the Ord furnace was hampered for a long time by trouble in obtaining stirring arms that would withstand successfully the high temperature of the furnace. Castings from some of the chrome-iron alloys possess the requisite strength and ability, but they are costly. The most favorable material is simple cast iron, but careful attention to its quality must be given. At Columbus the practice has settled down to cast iron for the arms in which the air makes the return circuit, and ferrochrome arms for those through which the air discharges into the furnace, these arms running hotter than the others with which they alternate.

The material for the stirring arms is not only important in connection with the Ord furnace, but also in all others, such as the Merton and Leggo, which are developments of the McDougall type. Consideration of this matter leads to a broad and illuminating classification of mechanical blende-roasting furnaces. This is as follows:

1. Those in which the rubbing mechanism is arranged to operate continuously and is contained entirely within the furnace. Such furnaces may be designed for the highest thermal efficiency, and, by virtue of the continuous operation of their rakes, the building up of hearth accretions is best counteracted. Furnaces of this type should roast with the minimum of coal consumption and the least use of labor. The chief drawbacks to them are the difficulty of maintaining the stirring arms and the tendency to make a high percentage of dust and deliver a dirty gas. The latter difficulty may be mastered by putting the gas through a Cottrell treater. These adverse conditions heretofore have stood in the way of the McDougall type of furnace for dead roasting.

2. Those in which the stirring mechanism is entirely comprised within the furnace, the stirring being effected by the rotation of the hearths, as in the instance of the Spiral. These also are well-designed furnaces from the thermal standpoint. It is difficult to keep the stirring devices in order, however, and, as compared with the McDougall type, they have the further disadvantage of difficulty of access to the interior. Furthermore, the peripheral motivation is mechanically more difficult and more troublesome than driving from a central shaft. On the other hand, owing to the shallowness of their roasting chambers, they do not make so much dust, while they give a richer gas.

3. Those in which the raking is intermittent, as in the Hegeler furnace. Owing to the intermittency, there is more opening of doors—therefore both the thermal efficiency and gas strength are impaired. Also owing to the intermittency, there are opportunities for the building up of hearth accretions, the removal of which not only entails additional labor but also adds to the impairment of the efficiency of the furnace.

4. Those in which the stirring mechanism is comprised only partially within the furnace proper. Such furnaces being necessarily designed with extensive openings to the external air, which can be but imperfectly sealed, or else being necessarily designed with large interior volume, are decidedly inferior from the thermal stand-

point, but mechanically are quite superior, therefore their upkeep is relatively low. These furnaces, however, are either incapable of design in muffle form, or else the muffle form, which may be workable, is unsatisfactory. The Brown straight-line furnace has been muffled and the Rhenania furnace has been mechanized, but neither of those attempts established itself in general practice.

There are some furnaces other than the simple McDougall type which would fall into the first class and which have had limited use and continue to be so employed. Such are the Merton furnace and the Leggo (used at Risdon, Tasmania), which may be described as long, multiple-hearth, muffle furnaces in which the ore is moved forward by a series of McDougall arms, the orbits of which overlap. These furnaces are fairly satisfactory thermally, but not so satisfactory as the Ord or Spirlet. The stirring arms are characteristically difficult to maintain and it is also difficult to keep such a system in alignment in a long furnace.

No very great attention need be given to the subject of furnaces for sulphate roasting. With them there is no question of utilizing the sulphur gas for acid manufacture, for the object is to utilize the sulphur for sulphating within the furnace itself. As the operation is conducted at a relatively low temperature, there is no such trouble with stirring mechanism as in the furnaces for dead roasting. Consequently, all of the electrolytic-zinc producers employ the modern McDougall furnace, or some modification of it, such as the Skinner furnace, which is used in Risdon in Tasmania. Of course, the ordinary Wedge furnace might easily be used for this purpose.

Several modifications have been tried in blende roasting and others may be. C. A. H. de Saullés introduced coal in mixture with the blende to be roasted, with the idea of effecting in the roasting furnace the reduction of metallic oxides other than zinc—which can be done at relatively low temperature—and thus of relieving the distilling furnace from doing that endothermic work and also minimizing the carbon dioxide resulting from such reductions, which diminishes the tendency toward formation of blue powder. This modification was practiced for a time at the works of the United States Zinc Co. at Blende, Colo., where about 8 per cent of anthracite fines was added to the charge in the last stage of roasting, care being taken not to let the temperature rise above the critical point of zinc oxide. All of this is theoretically sound, but it is doubtful whether the advantages exceed the extra costs and troubles. Anyway, the process has not spread.

A more promising innovation in blende roasting is to be found in the use of the Dwight-Lloyd sintering machine, which has been proved to be a cheap and effective desulphurizer, especially when following a preroasting in a furnace of ordinary type for reducing the ore to 8 to 10 per cent sulphur. Blende can easily be burned autogenously down to that point, following which the Dwight-Lloyd machine can carry on, without further use of fuel, and deliver a product desulphurized to 1 per cent or less. The product is moreover sintered, in which form it has been proved, at Port Pirie, South Australia, to be capable of quicker and more complete reduction and distillation than with the ordinary loose charge, all of which is in accordance with theory. A drawback to this method of blende roasting heretofore has been the inability to utilize the dilute sulphur dioxide gas from the Dwight & Lloyd machine. It has appeared recently, however, that such difficulty can be easily overcome by means of the Schmiedel process of making sulphuric acid, which seems to be able to deal with any kind of sulphur dioxide gas.

The Schmiedel process consists essentially in passing the gas through lead boxes of 7-cu. m. internal dimensions. The height of the box is just 1 m. and this dimension is highly essential. The box contains a bath of nitrated acid. Just dipping into the bath are a series of fluted rollers which are rotated in the direction of the travel of the gas through the box. The gas is introduced at one end of the box and is deflected downward by a water-cooled baffle plate. Passing under the latter it enters a rain of

acid introduced from the top of the box and then passes through a cloud of mist and drippings that is sprayed up by the rotation of the fluted rollers. With this severe exposure the sulphur dioxide of the gas is converted into trioxide and combined with water, producing sulphuric acid of about 78 per cent strength. The gas issuing from the box passes under a baffle plate at the outlet end and thence to a series of towers corresponding with the gay-lussacs of the ordinary chamber process.

Therefore, blende roasting in the future will probably be done either with the Ord furnace, followed by Cottrell cleaning of the gas stream; or with any good furnace of the McDougall type as a preroaster, followed by Cottrell installation, and Dwight & Lloyd apparatus as finisher, with both the preliminary and finishing operations delivering their gas to Schmiedel boxes for acid manufacture. Development along these lines is already well under way. Of course, it is possible that the poor Dwight-Lloyd gases may be led back into the preroasting furnace, in which their surplus of air will serve as the oxidizing agent. However, this idea is as yet untried in practice.

**Distilling Furnaces.**—Distilling furnaces of many designs are in successful use at present. It is even difficult to classify them and the following effort to do so differs from any other classification.

In the first place a distinction will be made between the method of heating and the metallurgical type, which is roughly equivalent to distinguishing between the inferior and the superior structure. Confining the attention for the moment to regenerative furnaces—and the modern furnace is almost necessarily restricted to this class—they may be either the countercurrent regenerative or the reversing regenerative. The latter may have regeneration for both gas and air or for air alone. The checkerworks may be arranged longitudinally, or transversely. In the laboratory, or combustion chamber, of the furnace the flames may rise vertically, leap over the middle wall, and descend on the other side, or they may reverse from end to end of the furnace, traveling longitudinally and horizontally. They may issue from ports in the middle wall. This is mainly a problem of efficient combustion and equable heating. The *desiderata* are a temperature of 1300 to 1550°C. around the retorts, as nearly even as possible, and a combustion product escaping to the chimney at only 200 to 300°C. as it leaves the furnace. There are designs, such as the Welzer (Overpett) and Neuruther-Siemens, that permit a ton of ore to be distilled with as little as 0.9 ton of coal. The best of the countercurrent furnaces and the Hegeler furnace so extensively used in the United States, in which the heat recuperation is effected through the medium of a waste-heat boiler, cannot equal that figure.

Metallurgically, distilling furnaces may be classified as Belgian, Silesian, and Rhenish. The distinguishing features are comprised within the superior structure, which may be combined with different forms of the inferior. Thus, a Rhenish top may be put upon a countercurrent regenerative base or upon a reversing regenerative base, or, indeed, the base may be simply designed for direct firing. The real difficulty is encountered in drawing a sharp definition among the three metallurgical types and especially between the Rhenish and the other two. This difficulty is not unnatural, considering the history of the types. Originally, there were only two types of distilling furnaces, *viz.*, the Silesian and the Belgian, which were quite distinct. Later there was developed a compromise, known first as the Belgo-Silesian and later as the Rhenish. Being a compromise, in which ideas were adopted from both the prototypes, the characteristic features of each were not everywhere borrowed to the same degree, and consequently there has always been some uncertainty as to just what constitutes the pure Rhenish type. The following is a generalization of the characteristics.

The Rhenish distilling furnace possesses a combustion chamber in which are suspended three double rows of retorts, so that the flames can circulate around all of them. The furnace has two façades, or fronts, and is roofed by a single arch springing

from the top of one front to the other. The support of the inner ends of the retorts is characteristically a vertical latticework of refractory blocks, but may be a middle wall, with ledges, as in the Belgian furnace. The retorts have the cross-section like a chain link, and are about 7 in. wide and 12 in. high inside at the maximum. The condensers are larger and longer than in the Belgian furnace. The front of the furnace is divided into closets completely enclosing the condensers, one closet comprising six condensers. The closets are subdivided by three horizontal shelves, which have holes through which the residues raked out of the retorts are dropped into pockets below the working floor.

As thus defined, the Rhenish furnace has the main design of the Silesian, and obtains much of the economy of the latter in labor and fuel, but it has the suspended retorts of the Belgian, giving the advantage of better heating. The dimensions of the retorts are a compromise between those of the Belgian and the Silesian and are as large as is consistent with the successful treating of high-grade ore, for reasons previously stated, and as long as will permit the load safely to be sustained. The retorts themselves are not a distinguishing feature of the Rhenish furnace, however, for the same retorts may be used in a Belgian furnace without destroying the distinct characteristics of the latter.

It has been mentioned that in Upper Silesia the Rhenish furnaces exhibit strongly some of the characteristics of the Silesian furnaces that preceded them, and oppositely in Belgium. Even in Rheinland and Westphalia, where the type originated, there have always been leanings one way or the other. Thus in some works, using retorts of the maximum height, the condensers are left in place during the maneuver, the residues being withdrawn from under them and the charging being performed through them, after the Silesian fashion. In other works using retorts of less height, such practice is impossible and the condensers have to be taken down according to the Belgian habit. In such respects, therefore, the Rhenish furnace offers no distinguishing feature. There are special furnaces, such as the Ferraris and the Ruck, which are even more difficultly classified. These have middle walls with ledges, deep embrasures, but not so deep as in the pure Rhenish furnace, and three rows of large retorts. They are, in fact, something between the Rhenish and Belgian, or it might be said that they are simply Belgians with three rows of retorts after the Rhenish fashion.

The Belgian furnace itself has undergone great modifications which have resulted in some confusion of description. The American zinc smelter in speaking of the Belgian furnace means the small, direct-fired blocks installed at Pittsburg, Kan., and vicinity about fifty years ago, which were abandoned about 1901 but were used again, ephemerally, during the war. The gas-fired furnaces used in the more modern plants he calls "Heglers" or "Siemens." A correct description would be "Old Belgian," "Hegeler-Belgian," and "Siemens-Belgian." The Hegeler-Belgian is simply a very high, gas-fired Belgian, turned over on its side. The Siemens-Belgian is an elongated Belgian, which was rendered possible by its method of gas firing. Besides such modifications the Belgian furnace may be equipped with either cylindrical or elliptical retorts, or even the large retorts employed with the Rhenish furnaces. Thus, the last were installed in the original Siemens-Belgian furnaces in this country, after the type of Aubry in France, but their use did not endure.

The distinguishing features of the Belgian furnace are the use of rather small retorts, arranged in four or five rows, each retort bridging from front wall to back wall (or middle wall, in a double furnace)—but especially in the design of the front walls. These are thin, being scarcely more than sufficient to support the front ends of the retorts. Outside of the front walls the structure is supported by an iron *devanture* of only small depth, the main function of which is to brace the furnace, while the horizontal shelves merely support the condensers and aid in clearing out the retort residues. Thus the front of the furnace is latticed off in a series of shallow pigeonholes instead of the deep closets of the pure Rhenish furnace.

The differences in fronts create a rather important difference in metallurgical operation. It was customary formerly to deplore the necessity for making the front wall of the Belgian distilling furnace so thin, which it was thought resulted in a terrific waste of heat by radiation. It was learned, however, from thermal computations, that this radiated heat was necessary in order to keep the condensers at the proper temperature. These computations received an illuminating confirmation in some electric-furnace smelting when it was found necessary to arrange an independent fire under the condenser. In the Belgian furnace the condensers project directly from the front wall of the furnace, and it is more difficult to regulate their temperature than it is in the Rhenish furnace, in which they are enclosed in closets, which often have adjustable, sliding doors in their fronts, causing the condensers to be in compartments which are really a part of the furnace.

However, as has been previously indicated, there are all kinds of departures from typical Rhenish design and practice. Thus, at Blende, Colo., the furnaces built originally as Welzers (Overpelt-Rhenish) were greatly modified later. While these furnaces have the deep closets, they came to be divided by iron plates instead of fire-brick tiling. The condensers fitted fully into the mouths of the retorts and, of course, had to be taken down during the maneuver. The discharging at Blende was eventually done by means of a machine, which demands free access to the retort, anyway.

Descriptions in detail of all the forms of distilling furnaces that had been constructed, and even of those that remain in use in Europe, would be tedious and useless. It appears almost as if every works metallurgist considered that he must design his own furnace. In the United States there has been much less originality, and consequently more uniformity. The following descriptions of furnaces in use will be confined to those that may be considered the standard forms.

In the United States the first distinction may be between the furnaces fired with natural gas and those that are fired with producer gas. All of them are Belgians. The natural-gas furnaces are mainly of the Hegeler type, *i. e.*, long furnaces in which the course of the products of combustion is longitudinal. The furnace is so piped, both for gas and for air, that the introduction thereof into the combustion chamber is distributed through ports through the pillars of the front, usually through every alternate tier. Thus a fairly equable distribution of heat is effected. Originally, these furnaces were built with an arrangement of retorts five rows in height. Occasionally, there were six-high furnaces, but they were rather rare, for their uppermost row was too high to be charged from the ground. The recent tendency has been to reduce both the six-row and five-row furnaces to four rows. A great many five-row furnaces survive, however. The five-row furnace usually has about 300 retorts per side. A four-row furnace may have the same number by being built a little longer.

A first use of natural gas in zinc distilling in the United States was in Indiana, where the furnaces were of the original Belgian type, and the natural gas was introduced at the bottom of the furnaces. Those works long since passed out of existence, but the works at Cherryvale, Kan., which continue in operation, were built with smaller but improved furnaces, and those continue in use. At Cherryvale the small furnaces are set end to end in triplets. Therefore, they have all the advantages of a long furnace in matters of mechanical operation, *i. e.*, continuous tracks are laid in front of them and the charging and metal drawing is done with the aid of cars, the three furnaces of a series being handled as a unit. In other words, the handling is just the same as if the ordinary long furnace were cut in three parts.

The labor upon natural-gas-fired furnaces is, of course, less than upon coal-fired, as there are neither coal nor ashes to be handled. In the distillation of the ordinary roasted Joplin blende the consumption of natural gas is about 40,000 cu. ft. per ton of ore.

If coal is to be used for heating the distilling furnaces, no one would nowadays think of using anything but gas firing for the production of the gas in standard form of gas producer, suitable to the particular coal which may be used. Thus the Swindell, Duff, Hegeler, Morgan, Taylor, Chapman, and Hughes producers are in common use. The distilling furnace itself is bound to be recuperative. The heat recuperation may be by means of the reversing-regenerative system, the counter-current system, or by steam-boiler attachment. At the works of the New Jersey Zinc Co at Palmerton, Pa., there were a considerable number of Convers-de Saulles furnaces, which were counter-current recuperative. They were an excellent development of the type. So also is the Schmidt & Degraaz, used in Europe. These furnaces at Palmerton have been recently displaced by the reversing regenerative type. Furnaces of this type give equable temperatures in their combustion chambers, but they are of inferior thermal efficiency and the maintenance of their flue systems is more or less troublesome. No extension of the use of this type of furnace is to be anticipated—at least not in the United States.

The majority of the smelters of the United States who use coal as fuel employ the Hegeler furnace. This is the conventional long furnace, with four or five rows of retorts, into which the gas is turned at one end and is burned by the gradual introduction of air from a central main, with branches coming down in front of some of the pillars of the furnace front, the air being delivered under pressure. Even so, there is apt to be a gradual decline in temperature toward the outlet of the furnace, especially if the length of the furnace be excessive, for the gas within the combustion chamber is constantly becoming more and more diluted with products of combustion and consequently less active. The tail end of the furnace is, therefore, the cooler part and it is, consequently, a common practice to recharge blue powder alone into the retorts of that part.

Because of the irregularity of temperature the zinc extraction in distillation with a Hegeler furnace is probably a little inferior. Thermally, the furnace alone is decidedly inferior, owing to the absence of direct means for heat recuperation. It is the common practice, however, to convey the escaping gases from the furnace through steam boilers. Therefore there is, in fact, a recuperation of heat through the medium of steam. How this compares with recuperation through the medium of air in a reversing regenerative furnace may be deferred until after the latter has been described.

At three works in the United States, viz., Peru, Dupue, and Rose Lake, Siemens-Belgian furnaces are used. These are long furnaces with an arrangement of retorts similar to that of the Hegeler furnaces, but commonly the Siemens-Belgian furnace has about 400 per side. In the base of the massive there are four regenerative chambers, filled with brick checkerwork, and extending longitudinally for the entire length of the furnace. The combustion chamber is divided by the conventional middle wall, with ledges, of the Belgian furnace, but it does not rise to the arch. The arch springs from the top of one façade to the top of the other. Originally, the gas and air were admitted through ports under the lowest row of retorts, but in later forms of this furnace, sometimes known as the Neureuther-Siemens, the channels are extended upward through the middle wall so that gas and air may be admitted through ports under some of the higher rows, a better distribution of the gas and air being thus effected. In operation, the gas and preheated air are introduced through alternating ports of one side of the furnace, and in burning the flames rise between the retorts, leap over the top of the middle wall, and descend between the retorts of the other side, escaping through its ports and thence through the regenerative chambers of this side, which are thus preheated. At intervals of 30 min. the direction of the gas currents is reversed. In these furnaces the temperature is fairly equitable. The two top rows of retorts run a little cooler than the three lower rows, and into them the blue powder is charged, but it is a common practice to mix some ore with the blue

powder and other between-products The Siemens-Belgian furnace has all of the mechanical advantages of any other long furnace It has a high thermal efficiency Even with the poor bituminous coal of Illinois the distillation of a ton of roasted Joplin ore is effected regularly with a ton of coal, and in the best work with as little as 0.9 ton of coal

The American Zinc, Lead & Smelting Co. has two smelteries in close proximity in Illinois, *viz.*, Rose Lake and Hillsboro, which are operated under similar conditions Rose Lake has Siemens-Belgian furnaces, while Hillsboro has Hegeler furnaces with steam-boiler attachments These two plants therefore afford an excellent comparison of the coal consumption of the two types of furnaces In order to make a comparison, each plant is debited with the amount of coal that has to be used for generating steam for power purposes, etc

	ROSE LAKE	HILLS BORO
Furnace fuel	1.00	1.60
Power and steam	0.50	0.10

Hegeler furnaces at other works give similar quotients of coal consumption Taking the requirements for steam into consideration, the Hegeler furnace is not so greatly inferior to the Siemens-Belgian as would appear at first sight It may be concluded, however, that it is something like 0.3 to 0.4 ton of coal per ton of ore worse than the Siemens-Belgian furnace and is somewhat inferior in the matter of zinc extraction On the other hand, the first cost of Siemens-Belgian furnace is much higher than that of the Hegeler and the cost of upkeep is also higher

In Europe a great many forms of old distilling furnaces survive In Belgium there are still some of the old Belgian type In Upper Silesia there are some of the old Silesian type The newer furnaces are generally of the Rhenish type The latter were first developed in Rheinland and Westphalia and were originally described as Belgo-Silesian In going over to the Rhenish type the Belgians give it their own coloring, so to speak and likewise do the Silesians With both of them, however, it is essentially the same furnace In it there are a good many works variations, but the most approved form at the present time is a reversing regenerative furnace with four checkerworks in the inferior structure two for gas and two for air These are arranged quarterwise *i. e.*, there is a pair of checkerworks for each end of the furnace instead of for each side, as in the Siemens-Belgians of the United States Consequently the course of the flames in the Rhenish regenerative furnace is endwise instead of sidewise

There are no suitable means for comparing the thermal efficiency of these two forms of furnace as there are no works in which the two have been in operation under closely parallel conditions A plant of Overpelt-Rhenish furnaces was built and operated for a great many years at Blende, Colo With these there was attained a low quotient of coal consumption, which was about 0.9 a figure identical with the best results with the Siemens-Belgian furnaces However Blende was operated on a different ore and with different coal from Depue

Anyway the thermal efficiency of the Rhenish regenerative furnace is high Eulenstein computed<sup>1</sup> the following heat balance of a Rhenish distillation furnace with Siemens regenerators

<sup>1</sup> *Metallurgie* 9 (1912) 328-333-396

Debit	Per cent	Credit	Per cent
Producer gas. . . . .	90.94	Heat in waste gas . . . . .	50.85
Sensible heat in charge	0.18	Heat in residue . . . . .	2.67
Burning of carbon . . . . .	8.74	Heat in spelter . . . . .	0.45
Sensible heat in new retorts	0.14	Heat in gas from condensers . . . . .	2.76
		Endothermic reactions . . . . .	10.96
		Sensible heat in discarded retorts . . . . .	0.19
		Loss by radiation and conduction by difference . . . . .	32.12
	100.00		100.00

Although the heat used for the endothermic reactions was only 10.96 per cent, the heat in residue, spelter, condenser gas, and discarded retorts, was exercised usefully, being inherent to the process. The total utilization of heat was, therefore, about 17 per cent. While that is very much inferior to utilization of heat in a steam boiler, it does not compare unfavorably with the utilization of heat in its transformation to mechanical power by means of steam boiler and engine. It must be remembered also that a part of the heat that is itemized as being lost by radiation is, in fact, required for maintaining the condensers at the proper temperature. It should be recognized, therefore, that the modern zinc-distilling furnace is not a discreditable metallurgical agency, although it may be freely granted that the old Belgians of the early days of zinc smelting in the United States, with columns of flame belched high by their chimneys, were quite disreputable, albeit picturesque.

Although the firing of distilling furnaces is mainly confined to the use of producer gas or natural gas, or perhaps in Europe to occasional relics of direct coal firing, the use of carbonaceous fuel in other ways is possible and in a few instances is practiced. The use of the waste gas from by-product coke ovens has often been suggested in zinc smelting. This is, of course, feasible, without any difficulty whatsoever. It has, indeed, been done by the Società di Montepioni at Vado di Ligure. In general, however, by-product coking plants occur in regions where there is more profitable use for their waste gas. The erection of such a plant for zinc-smelting purposes primarily is economically impracticable, for the coking plant will be considerably larger and more expensive than the zinc plant. In the coal fields of Mexico a unique condition exists in an extensive market for coke without there being any market for gas. The American Smelting & Refining Co. has taken advantage of this situation and has erected a zinc distillery to be fired with the waste gas.

It is possible to heat zinc-distilling furnaces by the combustion of powdered coal, although there would probably be great difficulty, if not impossibility, in applying coal in that form to regenerative furnaces. This method of firing has been introduced and practiced, however, at the Cherryvale works of the Edgar Zinc Co. The furnaces at this plant were originally designed for natural gas, which subsequently failed in supply. Powdered coal was then substituted, the coal suspended in the stream of air being introduced through the pipes that formerly carried the natural gas, with but slight modifications in arrangements.

Petroleum also may be used for firing the distillation furnaces, which has also been done at Cherryvale, Kan., and is now done at the works of the Società di Montepioni



at Vado di Ligure in Italy. The furnaces in use at the latter place were designed by Ermilio Ferraris and are unique in that they have regenerative chambers for pre-heating the air alone, the gas being delivered to the furnaces with the maximum of sensible heat when coal firing is employed, which implies setting the producers as near as possible to the furnaces and minimizing the loss by radiation between the producer and furnaces. In the latest designs petroleum may be substituted for producer gas or coke-oven gas, and it is possible to change immediately from one of these fuels to the other.

It is possible that the Ferraris furnace, which is ingeniously and intelligently designed, might be used for either producer gas, petroleum, or powdered coal. However, in order to have such latitude, a regenerative furnace would probably have to be designed with checkerworks or countercurrent flues for heat recuperation through the medium of air alone, as is the design of the Ferraris furnace. Undoubtedly, the design of this furnace has a good deal of merit, but its use has not spread outside of the works of the Società di Montepioni.

The electrothermic furnace need not occupy much attention, for as yet it has come into use only on a relatively small scale in Scandinavia. Theoretically, the electric furnace is bound to conform to the same metallurgical principles as the coal-fired furnace, with the practical difference that heating of the charge can be arranged internally instead of externally. The whole furnace may then become the retort and it is possible to increase very greatly the size thereof as compared with the retort that must be heated externally, with all the physical and mechanical limitations that obtain with respect to the latter condition.

The theory, as outlined above, is best exemplified by the electrothermic furnace and method of Dr C. H. Fulton, in which the ore and the carbon are mixed and pressed into small blocks, which are piled in a column upon the furnace hearth. A cylindrical bell, properly lined with refractory and non-heat-conducting material, is then dropped over the column, connection is made with the condenser, everything is made gas-tight, electrical connections are made, and current is passed through the column of charge, which heats by virtue of its resistance. When the distillation is completed, the bell is lifted and the residue is removed. While distillation is going on in one bell, another one is being made ready.

The Fulton process is, therefore, exactly the same as if distillation were being conducted in an ordinary retort set vertically and arranged for internal heating. It conforms absolutely to the theoretical conditions that cause zinc reduction distillation to be a two-stage process. The arrangement of the charge as a column of briquettes obviates the difficulty respecting egress of gas and vapor that is experienced with a column of loose charge. It gives, moreover, the advantages,—which are many—of a very dense charge. The Fulton process has given excellent results in experimental work. It has not yet been commercialized—it probably awaits an adequate mechanization.

All other electrothermic methods and furnaces have been in the field of zinc-lead smelting rather than of zinc smelting proper, the purpose being to treat mixed ores and obtain both zinc and lead as metals in a continuous process, scorifying the gangue and drawing it off as slag. The furnace is essentially only a box or covered pot, into which electrodes are introduced. The latter may develop heat by arcing between them, as in the original De Laval furnace, or by conveying current to the bath of molten slag, which then becomes a resistor. Or the electrodes, not quite touching the slag, may let their current arc to the slag, giving the arc-resistance furnace. There has been a great variety of designs, and in the handling of them there is an infinity of detail. The subject has been treated recently in a *Bulletin* of the U. S. Bureau of Mines on "The Electrothermic Metallurgy of Zinc," by B. M. O'Harra. The governing principles will be discussed later in this work.

**Accessory Apparatus and Operation.**—While blende roasting and the distillation of the calcined ore are the two main steps in the art of zinc smelting, there are many collateral things to be done, involving the use of a good deal of accessory apparatus and many supplementary processes. The ore and coal have to be crushed and mixed, the retorts and condensers have to be made, and there is a variety of apparatus for charging and discharging the retorts of the distilling furnace, drawing the metal, mixing and refining the metal, etc.

For crushing the ore and coal any of the standard machinery for those purposes is sufficient and no description of it is necessary. The quantity of such material to be handled annually is relatively small, even in a zinc smelter of great spelter output. Consequently, no great attention is devoted to this branch of the work and the crushing machinery that is used is apt to be of rather inferior type. A large proportion of the blende concentrates now arrive in such a state of fineness that no crushing is necessary.

For reduction material a wide variety of coals, short of straight bituminous, is used. Ordinary bituminous coal would be unsuitable, owing to its high percentage of volatile matter, it being undesirable to distil too much hydrocarbon in the zinc retorts. Bituminous coal, however, may be cindered or partially degasified, and then used, though the writer does not know of this being done in American practice. American smelters commonly use "dead coal," which is bituminous partially degasified by nature, semianthracite, Pennsylvania anthracite, coke, or a mixture of coal and coke. Whatever be the reduction material, it is desirable that it be low in ash and free from sulphur.

The mixing of ore and reduction material used to be done by hand in front of the furnaces. Then it became the practice to do it in a special mix house where a screw conveyor was made to serve as the mixer. Later mixers were introduced similar to those used for mixing concrete, which need not be described. European smelters still make extensive use of the Vapart mill, which is a centrifugal comminutor and mixer. In modern practice, zinc smelters always prepare their charge by mechanical mixing.

**The manufacture of retorts and condensers** requires a special factory, or pottery, as it is called, within the plant. In this the retorts and condensers used to be made by hand, then with the aid of rude machinery, and finally it became mechanicalized throughout. The selection of clay is a matter of great concern. Usually it is obtained from only a few places which have been proved by experience to afford the desired quality. American smelters use nothing but Cheltenham clay, which is dug in St. Louis, Mo. Clay arriving at the works is ground and then is generally allowed to weather, which improves its plasticity. Then it is ground again, wet, in edge runner mills. Raw clay and burned clay (called "grog" or "chamotte") are mixed in certain proportions, say half and half, producing the batch, so called. There may be introduced in the batch a certain proportion of old material, coke and silica—reground. The use of coke, up to 10 per cent, is general and desirable. It improves the density of the retort and its ability to withstand corrosion, and counteracts the formation of zinc spinel. Silica is added only if the ore to be distilled has a siliceous gangue, as such a gangue makes the wall of the retort most resistant against attack and increases the heat conductivity. In the distillation of Joplin blende the siliceous retort is excellent. For an ore with a basic gangue, of course, it should not be used, but rather a more basic clay.

The prepared batch goes to the pug mill, where it is thoroughly kneaded. The sausage from the pug mill is cut up and transferred to a hammering machine, in which it is consolidated into a ballot. The ballot goes to the hydraulic press. This system of making retorts was first introduced in Belgium. In borrowing it therefrom some American smelters omitted the hammering machine as being unnecessary. That may be so if the clay be very thoroughly densified by a pug mill. If this is not done any air remaining included is bound to impair the retort. Its effects may appear as blisters on the latter as they issue from the press.

The standard forms of press are the designs of Dor, a Belgian engineer. The elements of one, the more common, form are a heavy steel cylinder within which operate two concentric pistons. With both pistons down, the ballot of clay is thrown into the cylinder, the top of the latter being swung to one side. The top is then closed and the two pistons are moved upward together in order to press the clay into the top of the cylinder. The inner piston which forms the interior of the retort is then moved upward, while the outer piston moves downward. The top of the press is finally swung aside and the outer piston is moved upward, ejecting the retort through a die. The retort having emerged to the desired length, it is cut by means of a wire and received into an appropriate holder, wherein it is transferred to the drying room. The forming of the retort occurs under a pressure of about 200 atmospheres.

In another and earlier form of the Dor press the clay is fed into the bottom and is pressed through a die, the mandril of which is supported by a spider. The top of the press is closed and locked. The clay is pressed against the top, forming the butt of the retort. The top is then swung aside and the clay is forced up through the die, the butt having been previously made.

American zinc smelters commonly use the Wettengel and Simmonds presses, which are of American design and manufacture and possess many excellent mechanical features, but, essentially, they are the Dor press, Simmonds following the earlier form and Wettengel the latter.

In Europe, where the condensers are largely of the Rhenish and Silesian types, they are still manufactured generally by hand. In the United States, where nothing but the Belgian condenser of a simple conical form is used, the manufacture is now invariably by machines. The machines commonly used are the Garrison-Whipple and the Stafford. Both of these machines are similar in principle as well as in mechanism. They have molds of the exterior shape of the condenser supported vertically on a carriage, which can be revolved around a central axis. Each mold having been filled by a ball of clay passes in turn under a plunger shaped similar to the interior of the condenser, which is mechanically forced down, forming the clay. The condensers thus formed are removed from the molds and allowed to air dry from one to three days, after which they are trimmed. Sometimes they are left and used in the simple conical form. Sometimes they are "crimped," the larger end being contracted by pushing it into a sheet-iron form or ring, about 6 in. high. This crimping reduces the larger end of the condenser to the size of the mouth of the retort and also produces a bellying of the central part.

Both retorts and condensers must be carefully dried and finally burned before they are put into use. The retorts are dried slowly in hot rooms, in which they should remain for at least a month, but the longer the better. In American practice six weeks is a common time for seasoning, but even that is only a moderate time. Condensers are dried on shelves in open rooms for only a few days, following which they are baked for about 18 hr. in a kiln at a temperature of 900 to 1000°C. The seasoned retorts are taken as required from the dry rooms to the annealing furnaces adjacent to the distilling furnaces, in which they are baked at a temperature of about 800°C. for about 12 hr., the entire operation of loading, baking and unloading taking about 24 hr.

From the annealing furnaces the retorts are taken red hot to the distilling furnaces, in which they are inserted in place of the defective retorts that have previously been removed.

Various mechanical devices for facilitating the work in connection with the distilling furnaces have been introduced. Practically all furnaces have now one or two tracks in front of their façades to permit the operation of these devices. The simpler devices comprise a charging car, which is drawn down along the front of the furnace and from which the charge is taken directly for shoveling into the retorts. The blue-powder charge is, however, accumulated and spread out on the floor in front of the retorts in which it is to be put in the old fashion. The ladle, or kettle, into which the spelter is to be drawn from the condensers is carried on a truck, and is so adjusted that it can be raised or lowered. This truck is designed, moreover, with a shield to protect the metal drawer from the heat of the furnace along which he works. Similarly, another truck with a shield, and with rollers, corresponding to the rows of retorts, for support of the rabble is used in the work of withdrawing residues.

The withdrawal of residues is still done by hand by rabbles in a good many works. If the residue has slagged and become sticky, this is the only way of getting it out. When the residue is essentially dry, as it is ordinarily in the distillation of simple Joplin blends, it may be blown out by introducing an iron pipe connected with a hose and letting a little water issue from the end of the pipe, which is introduced in the retort about as far as it will go. The water is immediately converted into steam with explosive effect, which blows out the charge.

A good deal of attention has been given to the development of mechanical charging and discharging machines. Of the former there are two principal forms, *viz.*, the Saeger and the Dor-Delattre. The Saeger introduces the charge into the retorts tier by tier by inserting into the retorts devices on the principle of the screw conveyor and screwing the charge in. The Dor-Delattre machine throws the charge in by centrifugal force.

Among the discharging machines are the Saeger, the Simmonds, and the Rissman. The Saeger machine works on the same principle as the charger, but oppositely. The Simmonds machine introduces into the retort an endless rabble working over a sprocket. This is practicable only with a retort of considerable height, at least like that of the Rhenish furnace.

The several charging and discharging machines are practicable and have been introduced in numerous works, but in spite of some obvious advantages their use has not spread, owing to certain disadvantages, which may not be inherent in the machines themselves. Mechanical charging without doubt permits the denser loading of the retorts and more regular loading, *i.e.*, the charge per retort is not only put in to the maximum capacity but also all the retorts of the furnace are charged more nearly alike, both highly important considerations; moreover, there is certainly a saving of labor in the direct work. Similarly, in the use of mechanical dischargers there is a saving of labor and the retorts may be cleaned out better than by hand. All of these are important advantages. The disadvantages are that the machines are necessarily complicated and cumbersome and of large first cost. The common arrangement of American works, in which the distilling furnaces are set in parallel, is an obstacle. This involves a good deal of moving of the machines in order to get the charge, to shift from one to another, etc., and such handling is likely to offset all possible advantages. If the distilling furnaces be set end to end, as in European practice, it is easier to operate the machines down the line and to provide for mechanically filled supply hoppers near the several furnaces. In European practice, however, there is not the same incentive to mechanicalization as in America, owing to the relative cheapness of labor there. The present status of mechanically charging and discharging

may, therefore, be summed up in the words that the operations are mechanically possible, but America, for physical reasons, cannot economically apply them, and Europe for economic reasons does not need to

**Zinc-lead Smelting.**—Until about twenty years ago zinc distillation was conducted purely as a method of extracting zinc. The zinc distiller did not want to have lead in his ore and penalized it. This aversion still continues, to a modified extent, among zinc distillers pure and simple. With the advent of the great supplies of Australian ores, and other ores of similar nature, the zinc distillers of Europe, and especially of the Continent, overcame their dislike for lead, and, indeed, began to demand its presence to an extent of about 6 per cent as a minimum. Zinc smelting in Europe was, therefore, put practically upon a zinc-lead basis. The same thing was done by numerous smelters in the United States, but not to the same extent as in Europe.

It was formerly thought that lead was objectionable in zinc ore from the standpoint of destruction of the retorts, but analytical examination and consideration showed that such action was not to be feared. The real objection to lead is that it contaminates the spelter, but that is no very serious matter. Indeed, many galvanizers and rollers of sheet want some lead in their spelter and inasmuch as they buy spelter while the smelter buys zinc the lead content of the spelter is clear gain to him. If, however, too much lead goes into the spelter in addition to process, i. e., refining, is necessitated and the smelter does not want to incur that unless it be worth while. The zinc smelter, therefore, chooses between the alternatives of relatively little lead in the ore or else a good deal, an intermediate lead content being merely troublesome.

Lead is volatile, but its volatilization point (about  $1500^{\circ}\text{C}$ ) is so much higher than that of zinc (about  $920^{\circ}\text{C}$ ) that fractional distillation of the two metals is easy. The temperature in the retort does not attain that of the boiling point of lead. Nevertheless, even at  $1100^{\circ}\text{C}$  a proportion of lead is volatilized and entrained with the zinc vapor, condensing with the spelter. The higher the temperature of distillation the more lead is volatilized and entrained, and the lead content of a spelter is a rough index of the temperature at which distilled. At a given temperature the proportion of lead that is distilled is higher with an ore containing but little lead than it is with one that contains a good deal. It follows from this that, in order to make a spelter that is lead-free, or nearly so, by direct distillation, the ore also must be lead-free, or nearly so.

If the zinc ore be argentiferous and plumbiferous a portion of the silver is dragged over with the lead, but that is probably a mechanical entrainment to a considerable extent. It is certain that if zinc and lead distillation be conducted under the severest conditions as to temperature, as in electric-furnace smelting, to which reference will subsequently be made, no more of the silver and gold present in the ore will be volatilized than in ordinary copper blast-furnace smelting if there be a sufficient formation of copper matte to collect and retain the precious metals.

In distilling an argentiferous and plumbiferous zinc ore some of the silver and lead go over into the spelter, as previously indicated, but the major parts remain in the retort residue. The recovery of lead must, therefore, be made from both the spelter and the retort residue. From the spelter excess lead is ordinarily recovered by gravity settling, the spelter being conveyed to reverberatory furnaces for that purpose. At a temperature held as little as is practicable above the melting point of zinc, the latter is unable to hold more than about 1.5 per cent of lead and any excess of lead settles to the bottom of the furnace, whence it is drawn off separately. In the process of galvanizing when unrefined spelter is used there is an accumulation of lead in the galvanizing kettles, according to the same principle.

Spelter may also be refined by redistillation, which may be done either in clay retorts or in an electric furnace. During the war, when refined spelter commanded a very large premium, there was a good deal of refining by redistillation in clay retorts, but under ordinary commercial conditions that is an unprofitable operation. The only refining by redistillation that is done normally is that which is carried out in Scandinavia by means of the electric furnace, which is logically the last step of the Corneliuss process of electrothermic smelting, to which reference will subsequently be made.

The recovery of lead in the retort residues may be effected by passing the entire material to the lead-smelting blast furnace, or it may be subjected to mechanical concentration and the concentrate alone be smelted for argentiferous lead. When concentration is done, some of the surplus reduction coal is recovered. The choice of the method is determined by costs. Europeans generally concentrate; Americans smelt directly. The ultimate extraction of lead and silver from a zinc ore is about 50 to 75 per cent of the original contents, 62.5 per cent being perhaps a fair average.

The matter of lead recovery from a zinc-lead ore by the ordinary process of distillation can be but vaguely stated, however, as it is so intimately related with the original content of the ore and the manner of effecting the recovery. The main sources of loss are: (1) by volatilization during roasting; (2) by volatilization during distillation, a portion of which may be recoverable by refining the spelter; (3) in the tailings of the mill, dressing the retort residues; and finally there are (4) the ordinary losses of the lead-smelting furnace. As a debit against any lead that may be recovered under (2) is the cost of refining the leady spelter. Process (3) is a source of large loss and may be omitted, but then there is an increased weight of material to be treated by the lead furnaces and therefore a higher cost of smelting. Yet, here again there may be an offsetting condition, *viz*, the residues may be high in iron and the lead smelter may need iron. These few remarks will give an idea of the complexity of this subject, which is, indeed, incapable of accurate generalization. The only answer is that which is expressed in dollars and cents in each case. What applies to lead also applies to silver.

The best theoretical exemplification of zinc-lead smelting is to be found in work with the electric furnace. This is not a branch of electrometallurgy, but is of pyrometallurgy pure and simple. Electric energy plays no other part than supplying heat. Such generation of heat has the theoretical advantage of ability to develop it inside of the retort rather than outside, and at first sight this is an attractive possibility, promising the use of larger and more durable retorts and the best possible utilization of the thermal energy.

Much work has been done toward the development of smelting operations for the delivery of molten metallic lead and zinc vapor for condensation from the crucible of the furnace and from the top thereof as spelter. This is, indeed, practicable to a degree, but there is no good promise of making it a commercial operation. The condensation of zinc vapor as spelter, instead of as blue powder, can, indeed, be mastered by prereducing the charge and conforming to the theoretical conditions that have been set forth in a previous chapter; but lead cannot be delivered in a molten state from the bottom of the furnace except at a relatively low temperature within the furnace, which spells a high degree of scorification of zinc oxide and consequently a high loss of zinc in the slag. In other words, zinc reduction is a high-temperature process and lead smelting is a low-temperature process and it is impossible to reconcile these conflicting conditions in the same furnace. The only logical alternative is to operate the furnace under high temperature conditions and to volatilize both zinc and lead.

The last idea is the basis of the Corneliuss process, developed and practiced at Trollhattan in Sweden. The furnaces there are operated on the principle of producing

a highly siliceous slag, which commonly contains about 50 per cent of silica and creates conditions favorable to a high degree of zinc expulsion, *i.e.*, the percentage of zinc scorified and retained by the slag is relatively small. At this high temperature the lead of the ore is nearly all volatilized, likewise the zinc. Enough sulphur is left in the roasted ore to combine with iron and copper, which should be present, to form a matte and collect the precious metals. With an adequate matte fall the recovery of gold and silver in the matte is high. No attempt is made to condense the zinc as spelter. The vapor issuing from the furnace is cooled rapidly, the lead and zinc condensing together as a powder. This powder is delivered to an electrically heated rotating furnace, wherein the superficial coating of zinc oxide covering the metallic particles is rubbed off, and the metallic particles being thus rendered capable of coalescence are melted down as a very leady spelter. The latter is finally refined by redistillation in an electric arc furnace, but, of course, an ordinary grade of spelter can be produced by simple gravity refining. The ore-smelting furnaces at Trollhattan have now been built and successfully operated for large capacity, as much as 15,000 kg. of ore per 24 hr. being smelted in a single furnace.

The commercial practicability of the Cornelius process has been thoroughly demonstrated. It is not, however, of universal application, being greatly dependent upon cheap power and also upon the composition of the ore to be smelted. The furnace charge must be made up with a view to slagging the gangue of the ore according to the principles that obtain with all metallurgical processes of that type. If the gangue be self-fluxing, the cost of treatment will be relatively low, but if the charge has to be loaded with a good deal of barren flux in order to form the requisite slag the cost of smelting per ton of charge may be low while the cost per ton of ore may be high. The first cost of an electrothermic plant, with electric energy available for immediate delivery to it, is less per unit of capacity than for a coal-fired plant. Moreover, an electrothermic plant may be economically installed in smaller units. It would appear from these considerations that the application of electrothermic zinc-lead smelting is not likely to become general, but, rather, will be confined to places where conditions are particularly favorable.

In the earlier stages of electrothermic zinc smelting everybody experienced a common difficulty in the matter of condensation, an unduly large proportion of the zinc being condensed as blue powder. It is known now that that is inherent to any zinc-ore reduction and distillation process that is carried on continuously. The common process is conducted intermittently and in stages. In the first stage there is an expulsion of oxidizing gases. After they have been driven off, and when the effluent gas becomes essentially carbon monoxide, the temperature of the furnace is raised to the point of zinc reduction and distillation, and in such an atmosphere condensation of the zinc mainly as spelter can be effected. In a furnace operated continuously there can be no such control of gaseous conditions, and as fresh ore is charged into the furnace there is a constant development of oxidizing gases, and coincidentally there is more or less dusting. The entrainment of mechanical dust with the stream of gas and vapor constitutes an additional condition adverse to condensation of zinc as spelter. Electrothermic smelting requires, therefore, the conditions of a two-stage operation, just as there is in the common pyrometallurgy. With a continuously operating furnace there must be either a preliminary stage of prereduction in another furnace, or there must be a subsequent stage of blue-powder treatment, also in another furnace. Whichever be the choice, there are two stages or two steps. The Trollhattan metallurgists adopted the method of (1) reduction and distillation and (2) blue-powder retreatment. Other metallurgists have adopted the method of (1) pre-reduction and (2) distillation.

**Zinc Burning.**—In the distillation of zinc in a retort, whether the original source be zinc oxide to be reduced or crude spelter to be refined, the vapor is

condensed essentially as molten zinc if the proper conditions be maintained. If the vapor be quickly led into a large, air-tight vessel of sheet iron and quickly cooled, the zinc is condensed directly to a solid, finely divided form, *viz.*, blue powder. Instead of being condensed in a manner analogous to rain, as it is in the condenser of the spelter furnace, it comes down in a fashion analogous to that of snow. This is a commercial process for the manufacture of zinc dust, which finds a limited use in the arts as a chemical reagent and for some other purposes.

If zinc escapes condensation it burns at the gas outlet of the condenser, giving a greenish coloration to the flame and producing a whitish smoke of zinc oxide. If this happens in connection with the ordinary distilling furnace the smelter says that zinc is "burning." Instead of being burned accidentally, it may be burned deliberately for the production of zinc oxide. Inasmuch as this may be done, and practically is done, in a variety of ways, it seems best to describe this branch of zinc metallurgy as "zinc burning."

The original method of making zinc oxide was, in fact, done in just that way, spelter being vaporized in retorts, burned upon issuance therefrom, and the zinc oxide fume collected by settlement in chambers or by filtration through bags. This process is still practiced extensively for the manufacture of a superior grade of zinc oxide. Oxide, when produced in this way, especially from high-grade spelter, excels all others in purity, whiteness, fineness, and the other desirable physical characteristics. In Europe practically all of the zinc oxide is thus produced.

In America the bulk of the zinc oxide is produced directly from ore by what is known as the Wetherill process. If the ore be a simple zinc ore the product is zinc oxide. If the ore be lead bearing the product will be a mixture of zinc oxide, lead oxide, and lead sulphate, which is known in commerce as "leaded zinc." In either circumstance the metallurgy is essentially the same.

**The Wetherill process** consists essentially in reducing a mixture of oxidized ore and coal in a shallow bed resting upon an iron grate with small apertures, the air for combustion being introduced under pressure beneath the grate. With a loose charge a thin layer of coal is first spread upon the grate and when that has become ignited the mixture of ore and coal to a depth of about 8 in. is thrown upon it. A furnace is charged and worked off and the residues are withdrawn in about 8 hr. Therefore a normal rate of working is three charges per 24 hr.

The metallurgy of this process is relatively simple. The ordinary furnace charge consists of a mixture of 1 part of ore by weight with 0.7 to 1 part of coal. For the reduction of zinc oxide not more coal than one-eighth of the weight of the ore is required, the remainder of the coal being available, therefore, for the endothermic reaction. In this process there need be no consideration of surplus of reduction material in order to keep down the percentage of carbon dioxide, for the latter gas is wanted rather than not. The reduction of zinc oxide under these conditions is capable of being done with a high degree of efficiency as compared with the distillation for spelter.

In fact, zinc oxide is first reduced and the zinc volatilized, zinc vapor rising from the bed of the charge. This is immediately oxidized by carbon dioxide and burned by excess air. Therefore the space in the combustion chamber above the bed of charge is filled with bluish-green flames of zinc. The stream of gas issuing from the furnace carries zinc oxide with it. After passing through chambers for settlement of the dust it is conveyed through long cooling flues and finally is delivered to a bag house, in which zinc oxide is obtained by filtration.



As a metallurgical process for obtaining zinc oxide this is simple and essentially as above outlined. As a process for the manufacture of commercial zinc oxide for use as a pigment and as an ingredient of rubber, careful attention must be given to many conditions, both chemical and physical, discussion of which is outside of the scope of the present work.

For the manufacture of zinc oxide direct from the ore, two variations have been developed, which are known as the eastern Wetherill and the western Wetherill. In the western Wetherill, eight to sixteen hearths are grouped in a single furnace or block, the several hearths discharging their gas into a common combustion chamber in the upper part of the block. The eastern Wetherill furnaces are also built in blocks, but the hearths thereof are more like independent furnaces, each one delivering its gas into its own flue. There is more or less controversy respecting the relative merits of the two types, but, practically, the eastern Wetherill is confined to Palmerton, Pa., while the western Wetherill obtains in all the new plants in the West. It is probably the better all-round type and is best suited to the treatment of miscellaneous ores. In the eastern Wetherill there are a good many variations in the matter of furnace divisions.

In the operation of the Wetherill furnace of either type great care is necessary to insure an even passage of the air through the charge. There is a tendency for the air to seek out the places of least resistance and to form blowholes and craters, with uneven working as a result. In burning a loose charge, it is never possible to avoid such irregularities altogether.

The above description and comments relate to the standard form of the Wetherill process, as originally developed and still commonly practiced. In late years, however, the New Jersey Zinc Co. has introduced at Palmerton an entirely new process in so far as the furnace operation is concerned, this being an invention of its metallurgists. In the new process the ore and coal are made, under high pressure, into briquettes of double-pyramid shape and the furnaces are operated with such a briquetted charge instead of with a loose charge. The furnace operation is greatly simplified. Instead of its being necessary to operate with sealed doors, it is possible to operate the briquetted charge with open doors, the briquettes burning with the evenness and gentleness of egg-size anthracite on the grate of a fireplace in the house. Owing to this fact and also to the intimacy of the contact between the ore and coal, there is a noteworthy betterment in zinc extraction and a reduction of labor and other costs in the furnace operation, but of course, at the expense of the briquetting. The writer regards this process, which leads to an entirely different kind of furnace operation, as being a major improvement in the metallurgy of zinc.

Apart from its intrinsic merit, moreover, this process opened the way to the mechanicalization of the Wetherill furnace, which adds to further economies. All attempts to burn a loose charge on a traveling grate had been failures, and were bound to be so under former conditions, but the innovation of the briquetted charge, eliminating all trouble from blowholes, short circuits of air, etc., immediately made the traveling grate a possibility. The mechanical Wetherill furnaces have now been introduced at Palmerton on a large scale.

Another interesting and useful process of zinc burning consists of the use of the reverberatory smelting furnace, which was first developed on a large scale at Florence, Colo. The furnace is of the standard form for smelting copper ore, arranged for side charging. Matte and slag are drawn off just as in copper smelting. The ore, mixed with reducing coal, slides down upon the bath of slag, giving up its zinc on the way, while the residual gangue is scorified and flows into the slag.

The use of heating coal in this process is surprisingly small, being much less than for burning on the Wetherill grate and, in fact, but little more than for simple copper smelting. This fact can be explained only by the hypothesis that in this furnace,

in so far as the zinc is concerned, an endothermic reaction and an equivalent exothermic reaction occur contemporaneously. Zinc oxide is reduced at the expense of heat, the zinc is volatilized, and is immediately burned, surrendering the equivalent heat. Exactly the same thing happens in the Wetherill process, but in the latter the zinc vapor, which is removed promptly from the laboratory of the furnace, burns under conditions whereby its heat serves no useful purpose; whereas in the reverberatory furnace as developed at Florence it serves the purposes of the smelting operation.

In other respects zinc burning in the reverberatory furnace is subject to the same conditions that obtain in the smelting of any zinciferous ore, whether that be in blast furnace for lead or copper, in reverberatory furnace, or in the electrothermic furnace for zinc-lead smelting. The slag must be highly siliceous or calcareous or both in order to minimize the scorification of zinc oxide and thus avoid excessive loss of zinc in the slag. In the smelting at Florence a slag with about 40 per cent silica was made. Even so the scorification of zinc oxide was fairly high. In order to reduce that to a practical minimum it is probably necessary to make a slag with 50 per cent, or more, of silica, as is done in the Cornelius electrothermic process at Trollhattan.

The process of zinc burning in reverberatory furnace was originally developed at Florence as a means for getting zinc in a concentrated form out of low-grade ores. The zinc fume, which was impure, was sent to Keokuk, Iowa, for the extraction of its zinc by the electrolytic process. A similar furnace was more recently installed at Bully Hill in California, with a view to making zinc oxide as a commercial product. That attempt failed, owing both to excessive scorification of zinc oxide in the smelting and inability to collect a zinc fume of the requisite purity, notwithstanding successive refinings.

In the Wetherill process of making zinc oxide as a commercial product, principally for use as a pigment and as an ingredient of rubber, after the vapor leaves the furnace great skill in handling and a thorough knowledge of physical conditions are necessary. Much depends upon the avoidance of discolorations and also upon not only the fineness of the grains, but also their shape, the grains being so small that their dimensions are measured in decimals of a micron. That important subject may be here dismissed with merely the statement.

Another process of zinc burning is found in the extraction of zinc from old brass scrap, this being practiced at Carteret, N. J. The scrap is melted in a cupola furnace, the zinc volatilizing and burning and the fume escaping through the flue. A large part of it is obtained from cyclone collectors, through which it is made to pass, and the remainder from a bag house, which in this instance is operated mechanically.

The limitations of space make it impossible to go into the subject of bag houses and many other details of collecting zinc oxide fume. It may be said, however, that the bag houses that are commonly used are of the conventional type, employing cotton bags, from which the filtered fume falls into hoppers. The shaking is still done by hand. Mechanical shakers have been introduced, but they have not proved successful except in the small and peculiar installation at Carteret, nor have the forms of mechanical apparatus designed for continuous filtration, one or more of which have been tried by several smelters.

At the present time it seems that the Wetherill process is the only one that is suitable for making commercial zinc oxide directly from ore. Reverberatory smelting may economically produce a product ranging from off-grade to distinctly impure, which may be used as a source of zinc for the electrolytic process or as a source of zinc for the manufacture of lithopone and other chemical compounds.

**Electrometallurgy.**—Zinc is now being extracted commercially from its ores with the aid of electricity in two ways, viz., electrolytically and electrothermically. Both methods are of interest to the electrical engineer, in that they employ

electrical energy in great volume, but there the similarity ends. The electrolytic process belongs to the field of electrometallurgy. The electrothermic process does not, except by the broadest construction of terms. The electrothermic process is one of reduction and distillation and the principles that govern it are the same as those governing reduction and distillation by the common pyrometallurgical process. The main difference is in the manner of heating.

Electrolytic zinc extraction is based upon the electrolysis<sup>6</sup> either of a solution of zinc chloride or of zinc sulphate. The former was the first to come into commercial use, at Winnington, England, where it is still practiced. At that place the process is conducted in connection with general chemical manufacture, and the chlorine that is set free at the anode is utilized for the manufacture of bleaching powder. In the electrolysis of the sulphate solution the product of the anode reaction is sulphuric acid, which is utilized for the leaching of more ore. Although the chloride process was the first to be commercially introduced, no one would now think of undertaking anything but the electrolysis of zinc sulphate. This subject, however, is treated at length in another chapter.

In the present outlook the electrolytic process is not likely to displace the distillation on its own ground. It may do so, however, by the transferral of ore supplies from one place to another, just as a good deal of the ore of Broken Hill that formerly used to go to Europe for distillation now goes to Tasmania for electrolytic extraction. Or it may bring into the market zinc from ores that previously were non-commercial, such as the ore of the Sullivan mine in British Columbia. Anaconda makes a very large production of spelter from Butte ore, which formerly went to distillers in Oklahoma. Later it became unprofitable to get their zinc to the market via distillation in Oklahoma, but it was still profitable to do so via electrolytic extraction at Great Falls. It is, therefore, impossible to make any generalization respecting the competitive features of electrolytic extraction and distillation, for each case will be decided by its peculiar conditions.

As between the electrolytic and the electrothermic methods, any statement here must be limited to the broadest indications. In the electrolytic process the power requirement bears substantially a direct relation to the zinc content of the ore under treatment, for the power in the main is used directly for the electrolysis of zinc sulphate and is proportional to the amount of zinc deposited. In electrothermic smelting the condition is different, inasmuch as energy is consumed not only for the reduction of zinc oxide, but also for the reduction of other metallic oxides and the scorification of the gangue. As the percentage of zinc in the ore increases, the amount of other work that must be done in the furnace decreases, with the result that the readings of the wattmeter will not be proportional to the zinc production. In general, it may be said that the consumption of electrical energy in the electrolytic process will be less per ton of ore than in the electrothermic. However, the whole subject, together with economic comparison with the pyrometallurgical process, is too complicated to take up in a brief treatise.

**Refining and Uses of Zinc.**—An ill-advised attempt was lately instituted in commercial circles of the American zinc industry to abolish the use of the term "spelter" and substitute the term "slab zinc," principally because zinc had been commonly going under a nickname that was unworthy of it. In fact, zinc came into commercial use under the name of "spelter," which was derived from a Dutch word used for it in the Orient, where commercial production was first instituted. Moreover, there may be a commercial difference between zinc and spelter. The latter in its common form is an alloy of zinc and lead, together with more or less

cadmium, and is commercially desired to be such. In that respect zinc differs from copper and lead, both of which are always desired in a high grade of purity. Zinc, on the other hand, may be desired as high-grade metal or as common metal containing only 98 per cent zinc. It is correct, therefore, to speak of high-grade zinc and common spelter. In technology the term "spelter" is all but indispensable for the sake of precision of meaning without incurring the obligation of verbose circumlocutions and definitions.

There is a range of classification of commercial zinc and spelter, running from high-grade zinc down to Prime Western, or common, spelter. With the advent of the great supplies of high-grade zinc, the intervening classifications—intermediate, brass special, and selected—have lost a great deal of their significance. Only two terms are now in common usage, *viz.*, high-grade and Prime Western, the latter corresponding with the "good ordinary brands" of Europe. High-grade zinc is specified as containing not more than 0.07 per cent lead, 0.03 per cent iron, 0.07 per cent cadmium, and a total of impurities of not more than 0.1 per cent. All of the electrolytic spelters and the best-known brands of distilled spelters are well inside of those limits, most of them containing about 99.95 per cent zinc. Prime Western spelter may contain up to 1.6 per cent lead and 0.08 per cent iron, without any limit as to cadmium, which is likely to run up to 0.5 per cent.

The difference in the properties of high-grade zinc and common spelter are so strongly marked as to cause them to serve practically as two different metals. High-grade zinc is distinctly a soft metal. It may be drawn and spun and worked in ways that are impossible with common spelter. Common spelter is distinctly harder, giving a metallic ring when struck with a hammer, while high-grade zinc responds only with a dull thud. The difference in hardness is especially ascribable to the cadmium content.

The largest use for spelter is for galvanizing iron and steel. For that purpose a high-cadmium content is unobjectionable (unless it be a matter of galvanizing wire for telegraph and telephone purposes, for which its ability to withstand bending is essential) and the ordinary percentage of lead is also unobjectionable. Indeed, some important galvanizers have required this and instances have been noted where the producers of high-grade zinc have deliberately adulterated it with lead in order to conform to the wishes of their galvanizing customers.

For rolling into sheets, lead is also unobjectionable. By far the greater proportion of the sheet zinc of the world is rolled from leady spelter. In American mills sheet zinc is readily rolled from spelter containing 0.3 per cent cadmium. British rollers, however, find the presence of any cadmium beyond the limit of a few hundredths to be highly objectionable. This difference in opinion is ascribable, doubtless, to conditions in the rolling practice. In one case a large British roller contended that spelter with more than 0.02 per cent cadmium could not be rolled successfully. The answer given was that spelter with 0.3 per cent cadmium is regularly rolled in the largest American mills.

For brass making, which rivals galvanizing in importance, high-grade zinc is desirable, but before it became available on a large scale intermediate, special, and selected spelters were employed. For some kinds of brass a lead content is desirable. A high content of cadmium is unobjectionable in spelter for brass making, even for the manufacture of cartridge brass, as was shown conclusively during the war. No matter how high be the cadmium in the spelter, scarcely more than a trace of it goes into the brass.

For the other uses of spelter, some of which are growing greatly in importance, high-grade zinc is generally desirable or essential. It is essential for slush castings

and for the manufacture of oxide by the French process. It is essential also for the manufacture of die castings, a business that is growing in an important way. For the last purpose Horsehead spelter, a product of direct distillation, commands a premium over electrolytic spelter, although the two kinds of metal assay about the same in zinc. For some unexplained reason the Horsehead spelter is found to work the better.

It will appear from the above statement of uses and respective conditions that there is but little need for the refining of crude zinc. The spelter that is naturally produced goes directly to the use for which it is especially adapted. It was only during the World War, when the need of high-grade spelter for the manufacture of cartridge brass was far in excess of the natural supply thereof, that the refining of crude spelter became a great metallurgical industry. In normal times such refining is mainly confined to the reworking of dirty scrap, which cannot be merely remelted, and galvanizers' dross, which is highly impure by virtue of its high iron content.

The ordinary refining of crude spelter is merely a process of gravity separation for the purpose of dropping out an excess of lead. In the distillation of leady ore a considerable proportion of the lead goes over with the zinc and produces a first spelter that is rather high in lead. Such spelter is poured directly into a reverberatory furnace, or is remelted in such a furnace, and in that simple process excess of lead separates and sinks to the bottom, the capacity of zinc to hold lead being limited to a rather small amount, varying according to conditions of temperature, etc. By this simple process of refining, which is practiced generally in Europe and especially in Upper Silesia, the lead content of the common spelter (good ordinary brands) is reduced to about 1.25 per cent. This process has the further advantage of yielding a uniform spelter, for in the melting furnace it experiences a thorough mixing. As drawn directly from the condensers of the distilling furnace there is a considerable variation in the composition, according to the conditions of temperature, etc. that obtain in individual retorts, which vary in different parts of the furnace.

American zinc smelters do not generally refine in this way, although it was formerly done at Blende, Colo., not being constrained to do so by virtue of the lead content of their spelter. It has been suggested, however, that they might advantageously do so just for the sake of insuring uniformity of their product. American smelters, however, do a certain kind of refining by selection, *i. e.*, keeping separate their several draws of metal. Thus the first draw, distilled at the lowest temperature, is naturally lowest in lead and highest in cadmium, and, consequently, marketable as spelter for brass making; while the later draws, lower in cadmium and high in lead, go to the galvanizers as common spelter. This practice is less general now than it was before the advent of the great supplies of electrolytic spelter which have largely captured the brass trade.

When the problem is to refine crude spelter so as to produce a product very low in lead, that must be done either by electrolysis or by redistillation. The electrolytic refining of crude spelter using a zinc sulphate electrolyte is easily practicable, but generally will be unprofitable inasmuch as no by-products are recovered and the only useful purpose is to improve the grade of the zinc. This process of refining was done at Baltimore during the war, but ceased promptly with the disappearance of the premium for high-grade spelter. Anyway, this process was never practiced on anything but a small scale. On the other hand, refining by redistillation became a large industry.

Refining by redistillation was performed by charging sticks of crude spelter into the retorts of an ordinary distilling furnace, putting a dam in the mouth of the retort, or in the inner end of the condenser. Or else the retorts were reset so as to give them an upward inclination instead of the regulation downward, in which event no dam was necessary. Or else special furnaces were built with a single combustion chamber, giving access to both ends of the retorts, so that, while zinc vapor passed into the condensers from the upper end, lead could be tapped off at the lower end.

These furnaces were heated to only a little above the boiling point of zinc. They were provided with condensers larger than the ordinary in order to take care of the great flow of zinc vapor, and they were drawn frequently and were otherwise handled in conformity with the altered conditions as compared with ore distillation. They yielded a spelter with 99.85 to 99.9 per cent zinc, the major impurity being cadmium. The percentage of zinc condensed as spelter was, of course, much higher and the percentage condensed as blue powder was much lower than in ore smelting. A common ratio of condensation as spelter was 80 per cent. The loss of zinc in the process was from 7 to 10 per cent, which was due to absorption and failure to condense, the loss in residue being, naturally, but little. Obviously, no such loss could be faced except with the compensation of a premium more than offsetting the metal refined and recovered, and with the disappearance thereof this metallurgical practice quickly died.

At the present time refining by redistillation is done only in connection with the excessively leady spelter of the Corneliuss process (Trollhättan), for dirty scrap and junk, and for galvanizers' dross. The Scandinavians use the electric furnace (De Laval, or arc, type) for this purpose. In this country the ordinary distilling furnace is used, as at Donora, Pa., or the special furnace of the secondary smelters pure and simple.

The last is a central chimney with a series of fire boxes, commonly eight, grouped circumferentially around it. Each fire box has its grate and above that a pear-shaped graphite retort, about 36 in. long and 20 in. in diameter at the belly, holding about 700 lb. of dross. The retort, which is set at an upward slant, discharges its vapor into a condenser slanting downward in the regular way. The distillation of a charge requires 18 hr., about 2 lb. of coal per 1 lb. of dross, and the labor of one man per shift per four retorts. The retorts last for forty to sixty charges. Spelter of excellent grade is produced.

When spelter was being refined by redistillation on a large scale in this country, some curious residual products were obtained, especially gallium, indium, and germanium—elements that never appear in ordinary analyses of spelter, although their occurrence in zinc ores has been occasionally detected. The experience in Oklahoma during the war showed that they exist in the ore of that district, that they distil over with the spelter at the temperature of the ore-smelting furnace, but that they do not redistil at the temperature of the refining furnace. The presence of infinitesimal proportions of one or more of those elements may possibly explain certain differences between high-grade spelter produced by direct distillation of ore and that which is produced by electrolysis.

In general, it is quite easy to refine crude spelter from lead by distilling at low temperature. Not so with cadmium, which can be eliminated only by cutting out a preliminary draw or two in which it will be concentrated. Iron as an impurity in spelter is the result of bad handling. It may come from the iron tools that are used, from drawing ore into the condenser, or from letting spelter in the condenser back up into the retort. The ore in the retort will contain more or less reduced iron, if it be at all ferruginous, and the spelter may be contaminated by contact with it.

There is a growing tendency in American manufacturing industries that use spelter to dismiss the old gradings of the metal and specify the percentages of lead and cadmium that have been found to give the best results for their particular purposes. What are commonly called impurities may, therefore, be desirabilities in some instances. Thus cadmium is sometimes deliberately introduced into high-grade spelter. An advantage of the latter is, of course, the ability to produce from it any composition that may be wanted and to do so unerringly. The idea, however, that high-grade spelter cannot be used in its purity for galvanizing is rather nonsensical.

## CADMIUM

BY DONALD M. LIDDELL<sup>1</sup>

**Cadmium has practically no metallurgy**, except as a by-product of zinc. In the main its recovery depends on its greater volatility as compared with zinc, and on the fact that zinc precipitates cadmium from solution.

One method of cadmium recovery has already been spoken of,<sup>2</sup> involving the use of electrolytic-zinc plant solutions. Other sources of cadmium supply are: Flue dust from blende roasting; condensed fume, blue powder or zinc dust from zinc distillation; tank residues from lithopone manufacture; electrolyte from electrolytic lead refining, and fumes from lead furnaces.

**Pyrometallurgical Methods.**—The original Silesian practice was to redistil a rich-cadmium blue powder, using prolongs on the condensers, which were removed as soon as the flame ceased to have the brownish tinge characteristic of CdO. The blue powder was mixed with about 50 per cent of coke breeze and the product from a 4 per cent Cd blue powder would run about 38 to 50 per cent Cd, while if the original blue powder ran 6 to 8 per cent Cd, the powder in the prolong would run about 75 per cent Cd. The retort must not be run too hot. This prolong condensate was then mixed with about 40 per cent of its weight of charcoal or 60 per cent of its weight of coke breeze and charged in a cast-iron retort heated by the waste gases from the regular zinc furnace. The product of this redistillation was caught in an iron condenser and was practically pure cadmium.

**Wet Methods.**—These mainly depend, as already stated, on the fact that zinc will precipitate cadmium from solution, and to a less degree, that zinc can be removed from a cadmium-zinc sulphate solution by agitation at 60°C. with Zn or Zn(OH)<sub>2</sub>, following by cooling to 35°C., at which point basic zinc-sulphate precipitates.

The electrolytic zinc producer is constrained to precipitate cadmium from a sulphate solution as a purification preliminary to the electrodeposition of zinc. This precipitation is effected by the addition of atomized zinc, which throws down cadmium, copper, and other impurities, including arsenic, antimony, cobalt, etc. There is obtained thus a mixed precipitate, enriched in cadmium. Further treatment of this precipitate separates the copper and cadmium, both of which are eventually recovered. The most convenient way of getting the cadmium is by electrodeposition from the purified solution of cadmium sulphate. The electrolytic zinc producers are now the largest suppliers of metallic cadmium, and owing to the advent of their new supplies, which has happened only within the last two years, the market price for cadmium has fallen greatly.<sup>2</sup>

In the treatment of cadmium-bearing lead blast-furnace fume, the fume is mixed with its own weight of 60 deg. sulphuric acid and heated until fumes cease to come off. It is then leached with spent electrolyte with air agitation (to oxidize all ferrous to ferric compounds). The leach is then neutralized with slaked lime, throwing out Fe<sub>3</sub>(AsO<sub>4</sub>)<sub>3</sub>, Zn(OH)<sub>2</sub>, and PbSO<sub>4</sub>. The copper is then thrown out by Na<sub>2</sub>S, and the resulting solution, which should be concentrated to 8 per cent Cd and 1 to 2 per cent

<sup>1</sup> Wald & Liddell, Engineers and Economists, 2 Rector St., New York.

<sup>2</sup> See p. 1120

$\text{H}_2\text{SO}_4$ , is electrolyzed using aluminum cathodes and corrosion anodes, with a current to 5 to 8 amp. per sq ft. and about 3 volts tank potential.

Thallium, if present, can be removed from a neutral cadmium solution with potassium chromate. This is a very important reaction.

The treatment of bag-house dust from lead furnaces at Denver, Colo., is thus described. About 300 lb. of dust is heated in an iron pan with 120 lb. of 60 deg. acid for four days in a flue at  $230^\circ\text{C}$ . The resulting cake is crushed to quarter-inch size and heated in iron pans for 48 to 60 hr at  $325^\circ\text{C}$  and the resulting powder leached with water. The arsenic in this solution is then determined by analysis and 10 lb. of bluestone added for each pound of arsenic present. The copper-arsenate precipitate is then removed and the excess copper thrown down with scrap iron and a little sulphuric acid. The cadmium is then thrown out of solution on zinc bars immersed in solution and the precipitate scraped off the bars and melted.

**Properties.**—The boiling point of cadmium is  $785^\circ\text{C}$ . at 760 mm. pressure compared with  $906^\circ\text{C}$ . for zinc. The melting point of cadmium is  $320^\circ\text{C}$ . Its specific gravity is 8.604 cast; 8.694 hammered. The specific heat is about 0.057. Some of the fusible ternary and quaternary alloys are given in Chap II. The ternary alloy of Cd, Pb, Sn and Bi of lowest melting point (about  $70^\circ\text{C}$ .) is 10 10 Cd; 27 27 Pb; 13 13 Sn, and 49 50 Bi. Lipowitz metal is 10 Cd, 26 7 Pb; 13 3 Sn; 50 Bi. If 30 parts of Lipowitz metal is melted with two parts of mercury the result is a compound melting at  $37^\circ\text{C}$ .



## CHAPTER XXXV

### METALLURGY OF QUICKSILVER

By MURRAY INNELS<sup>1</sup> AND H. W. GOULD<sup>2</sup>

**The metallurgy of quicksilver** is very simple, most writers on the subject say, beginning with Agricola in his treatise on Metallurgy in 1554. Though simple in outline, however, there are certain qualifying conditions which render its practical application somewhat difficult as to details.

The metallurgical process is one of simple distillation by applying heat followed by condensation in a cooled confined space. The boiling point of mercury is variously given by different authorities as between 355 and 360°C, at which point it is converted into a colorless vapor, the density of which is given as between 6.7 and 7.03.

Generally speaking, there are two main types of quicksilver reduction—the closed retort, where the ore is placed in an iron pipe or receptacle and fired externally, and the quicksilver furnace, where the heat comes in direct contact with the ore and the gases of the fuel combustion combine with the volatilized mercury.

**Retorts.**—Quicksilver retorts are not used in any of the large quicksilver mines in Spain and Italy and, on account of their small capacity, are only used in this country on prospects or, in some instances, to burn soot from the condensing plant of the large furnaces. Only a mere fraction of the total reduction of quicksilver is made from retorts.

Two types of retorts are in general use in this country—the round pipe, called the Johnson McKay, and the “D” retort.

The Johnson McKay is most commonly used. It is a cast-iron pipe 12 in. in diameter by 6 ft. 6 in. long and 1 in. thick. This is cast with a bell end, allowing for two cast-iron lids that are luted on with ashes. These retorts are put up twelve or less in a bench with a fire box on one end, with the heat passing in flues under the pipes and back over them to a stack. On the opposite end from the bell a 3-in. pipe leads out and down on a slight inclination to a trough. This pipe is the condenser. The ore is charged in the pipe with a scoop, about 200 lb. to the pipe. The lids are luted on and the ore is roasted from 8 to 12 hr., at which time it is drawn and recharged. The heat maintained in the pipe ranged from 700 to 1200°F and, as the mercury is volatilized from the ore, it passes out through the condensing pipe and drops into the trough.

Where much sulphur is present, lime is generally charged with the ore. According to Bradley,<sup>3</sup> retorting “depends upon heating the mercuric sulphide with lime when the sulphur combines with the calcium, forming calcium sulphide and sulphate, while the mercury is liberated, as shown by the equation



The capacity of a twelve-pipe Johnson McKay retort ranges from 2 to 4 tons per 24 hr.

<sup>1</sup> Consulting engineer, San Francisco, Cal.

<sup>2</sup> Consulting engineer, San Francisco, Cal.

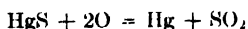
<sup>3</sup> “Quicksilver Resources of California” *Bull.* 78, p. 209.

The "D" retort is a heavy, cast-iron pipe, it has a cross-section like the letter "D," but with the straight side lying horizontally. These retorts are generally made about 18 in. wide on the bottom, 12 in. deep in the center, and 6 ft. long, and have a condenser pipe leaving somewhat similar to the Johnson McKay. Generally, the ore is charged in sheet-iron pans, two or four to the retort, a complete charge being about 400 lb. The retort has a capacity of from 800 to 1,000 lb. per day. The "D" retort may be erected singly or in banks up to four or six. Only a few of these are in use at the present time.

Generally, retorting is very unsatisfactory on account of the very small tonnage they treat, the large amount of fuel consumed per ton of ore treated, and the possibility of salivation of workmen. As stated before, they are generally used for development work on prospects.

**Furnaces.**—Just when retorting gave way to the furnacing of quicksilver ores on a large scale is not definitely known, though it is known that crude shaft furnaces were in use at the Almadén mine in Spain as early as the twelfth century. After the discovery of America, and with the heavy working of gold placers and silver mines in South America and Mexico, the demand for quicksilver was greatly stimulated, and most of the production came from the Almadén mine in Spain, and later from the Huancavellica mine, in Peru. It was at this latter place in 1634 that Don Saverda Barba developed a very efficient furnace that was introduced into Spain in 1646 and became known as the Bustamente furnace. Ten of these plants were installed from 1646 to 1654 and all of them are still in operation at the present time. These were shaft furnaces, intermittently charged, fired, and drawn, and, though they look very crude today, they probably have, in their 275 years' existence, produced more quicksilver than any other type of furnace. As they have been described many times, it is unnecessary to go into their construction or operation, nor to describe the many types of furnaces that have been built, tried, and forgotten in bygone days.

In furnacing quicksilver ores the heat is applied directly to the ore in the presence of air, the oxygen in the air combining with the mercuric sulphide, forming sulphur dioxide and freeing the mercury in accordance with the equation



The furnace in most common use today in Europe—both at Almadén, in Spain, and at Monte Amiata and Idria, Italy—is the Cermak-Spirek, generally called the Spirek furnace, from which the bulk of the European production of quicksilver is made. This is made both as a shaft and as a tile furnace—the shaft furnace for treating the coarse ore (1½ in. +) and the tile for treating the fine. In the coarse-ore furnaces the fuel, charcoal or coke, is charged with the ore and, generally speaking, they are very efficient. The same can be said of the Spirek tile furnace, of which some thirty installations, ranging from 12 to 24 tons per day, are now in operation in Europe.

However, as much has been written about these furnaces by European writers, the details of their construction or operation will not be discussed here. A particularly good description of European quicksilver-reduction plants has been written by Dr. Roland Sterner-Rainer in 1914.

The practice in Spain is still very antiquated. No apparent effort is made to cut reduction costs, when such a plan would in any way reduce the number of men employed, as the mine is government owned, and very much in politics—therefore as many men as possible are carried on the payroll. With high-grade ore (7 to 8 per

cent), however, quicksilver is produced at a comparatively low cost per flask, but under the conditions not much improvement in metallurgical practice can be expected.

As a comparison, the Cloverdale mine, in Sonoma County, California, operating a rotary furnace, roasts 90 tons of ore per day with one man on a shift (three men per

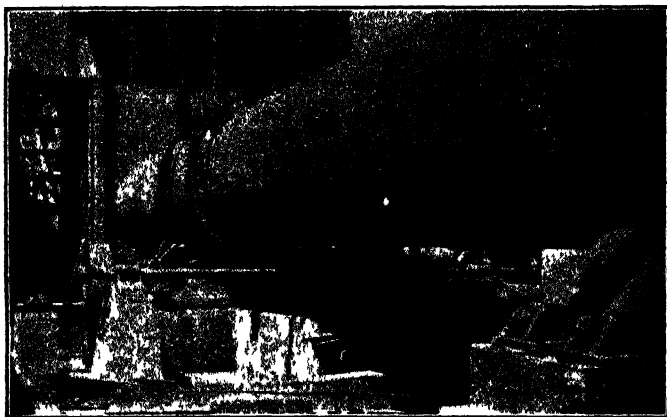


FIG. 1.—Gould rotary furnace, 5 ft by 56 ft, at New Idria



FIG. 2.—Spirek condensers at Monte Amiata

day). At the Almadén mine, in Spain, fourteen furnaces roast 78 tons and some 600 to 800 men are employed in the operation.

Another instance is the Abbadia San Salvatore mine, at Monte Amiata, in Italy, where over 400 men handle 278 tons in eight Spirek fine-ore and fourteen Spirek coarse-ore furnaces. As compared to this, at the New Idria mine, in San Benito County, California, five rotary furnaces will roast 400 to 500 tons per day, if run to capacity,

requiring only 10 men per day. The main reason for this is the low cost of labor in Europe as compared with the United States

Previous to 1914, the largest and most up-to-date plant in Europe was at the Idria mine, in Carniola (at that time in Austria, but now in Italy). The mine was then

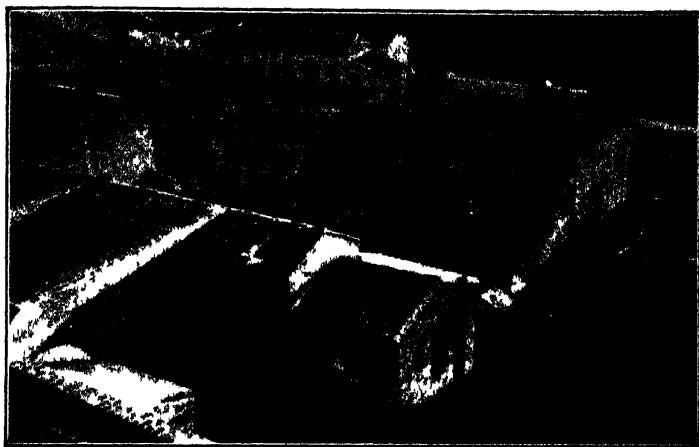


FIG. 3—Bustamente furnace

owned and operated by the Austrian Crown and much attention was given to the development of new metallurgical practices. Much that was written before 1914 on quicksilver metallurgy came from this source. It was here that the Lach, Kroupa, and Cermak-Spirek furnaces and the Spirek condensing system were developed.

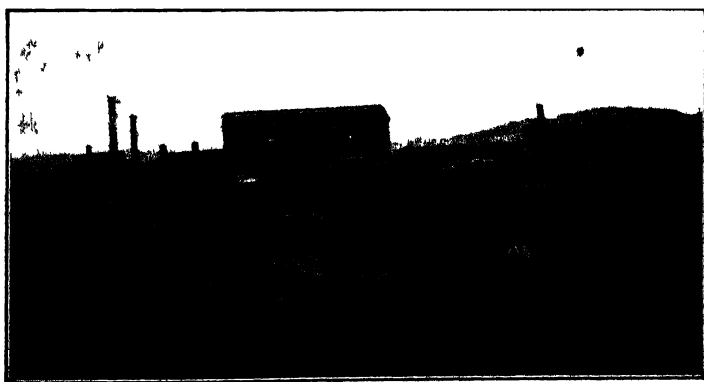


FIG. 4—Reduction plant at Almadén, Spain

In the United States from 1850 to the early seventies, practically all of the quicksilver treated in this country, which at that time meant California, was handled either in retorts or small shaft furnaces—the greater part in the latter. The most successful of these was probably the Knox-Osborne, which was patented in 1872, and at one time there were several of these plants in operation in California.

As the mines developed deeper, more fine ore was mined and the necessity for fine-ore furnaces increased. Among the early fine-ore furnaces developed was the Liver-

more—an incline furnace—of which several installations were made, including two at the Almadén mine, in Spain.

In 1875 and 1876, H. J. Huttner and Robert Scott developed at the New Almadén mine in Santa Clara County, California, what became known afterward as the Scott

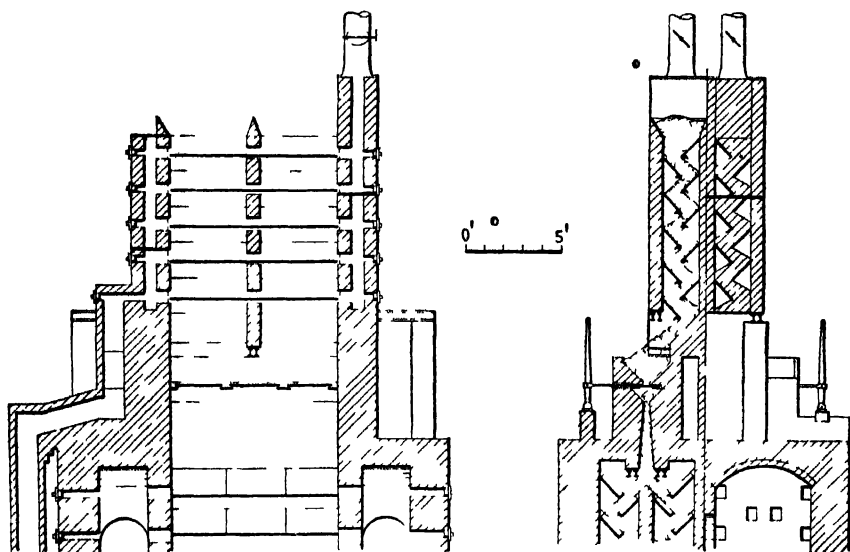


FIG. 5 —Oat Hill dryer top

furnace, and which in a short time practically superseded all other furnaces in this country, except in a few instances where coarse-ore furnaces were used. These furnaces have produced the major portion of quicksilver in the United States. Scott built these furnaces all over the United States and Mexico from 1876 until his death,

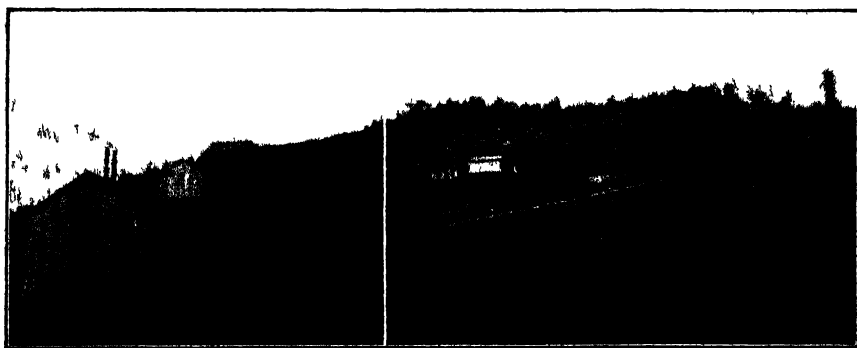


FIG. 6 —Oat Hill Plant left to right, furnace building, ore bin, cooling unit, brick chambers, flue, and stack

in 1918. The Scott furnace is what is commonly known as the tile or shelf furnace and ranges in capacity from 10 to 60 tons per day. The capacity is governed by the number, length, and height of the ore chambers, each additional tile increasing the length of the chamber by 36 in. and the height varying with the number of tiles

placed one above the other. The opening, or shelf slit, between the edge of one tile and the face of the one next below it was originally set at 3 in. This has been widened in later furnaces up to as much as 8 in., but was usually 4, 5, or 6 in., so that medium-sized ore up to 3 in. may be treated in these furnaces. As denoted from the drawing, the tiles form a zigzag channel for the passage of the ore from the top to the bottom of the ore chamber. The tile used are flat, generally being 3 by 15 by 36 in. in size. The tile ore chambers are increased in heavy outer brick walls, braced with iron tie rods. Peep holes are placed in the end walls to enable observation of the condition of the ore in different levels in the furnace.

Scott made many refinements in the design of his furnace during the years of his experience in building plants. As an example, the last plant built by him—a 40-ton furnace at the Oat Hill mine, in Napa County, California, will be described. In this plant was incorporated an ingenious ore drier, described by C. N. Schuette in 1919.

The Oat Hill plant was erected during the latter part of 1918. The decision to erect a tile pipe-condenser system was based on the result of experiments conducted by the U. S. Bureau of Mines at the Oceanic quicksilver mine and at the Berkeley Experiment Station, and its construction was supervised by Mr. Innes. Data for this report were obtained in February, 1919, when the plant was in full operation. \*

**General Description of Plant.**—The furnace was built on the foundations of a former furnace, in an excavation about 20 ft. below the surface of the ground. The condenser system is built on three terraces behind the furnace. The furnace gases pass from the furnace to a brick condenser built directly behind the furnace on the lowest terrace. From here the gas stream turns to the right and passes to the tile-pipe cooling unit on the second terrace and from there to two brick chambers on the third terrace. From here four flues of 1-ft. tile pipe lead the gases to a 25-ft. stack, situated about 30 ft. higher and 150 ft. distant.

The burnt ore is trammed to the dump through a cut, giving access to the ground level of the furnace.

An ore bin is situated directly behind and above the furnace and ore from it is trammed directly into the hopper of the drier.

**The Scott Furnace and Ore Drier.**—The furnace is a standard three-tile Scott furnace. The method of tying the furnace is an improvement over the customary method. Six-inch angle irons are placed over the corners, and 6-in. channel irons are placed at the intermediate points of support. The tie rods pass through holes drilled in the angle irons. This system of tying the furnace is neat and effective and was adopted at the suggestion of Mr. Innes.

The drier simulates the furnace in design, iron plates replacing the tile. It is built on the furnace between the throats. The hot air for drying the ore is obtained by heating air with the heat of the spent ore in the draw, which is carried to the drier through two brick chimneys at the rear of the furnace.

It was necessary to change slightly the design of the ashpit of the furnace in order to obtain the hot air for the dryer. The ash pit of the furnace was divided into an upper and a lower part by a cast-iron plate.

The ash can be dropped into the ash pit proper, by hoisting it, at intervals, through an opening near the door, which is closed by a sliding door.

The iron plate which divides the ash pit cuts off the lower six flues or gas passages through the furnace, and is on a level with the floor arch of the lower rear dust chamber. Air entering through the door of the ash pit is heated by passing through the flues formed by the tile and hot rock, and passes through the "rear ash

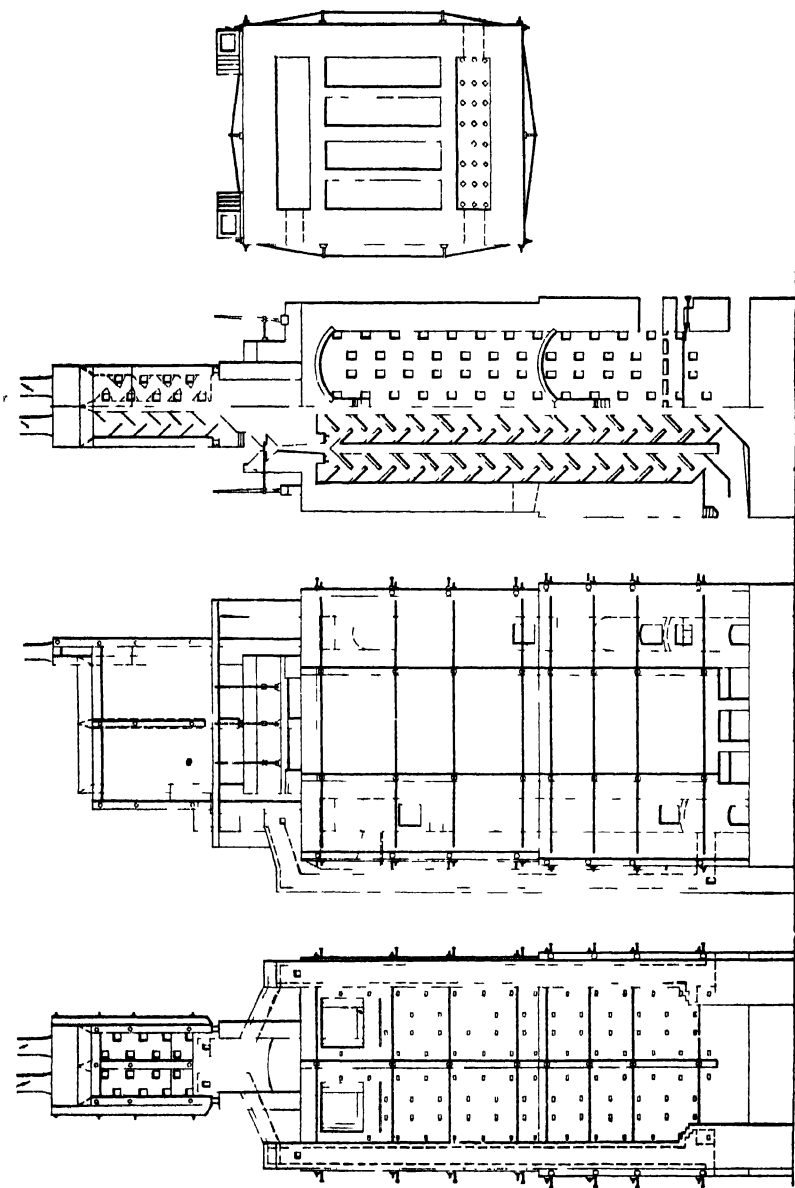


FIG. 7 —Scott furnace and ore dryer at Oat Hill.

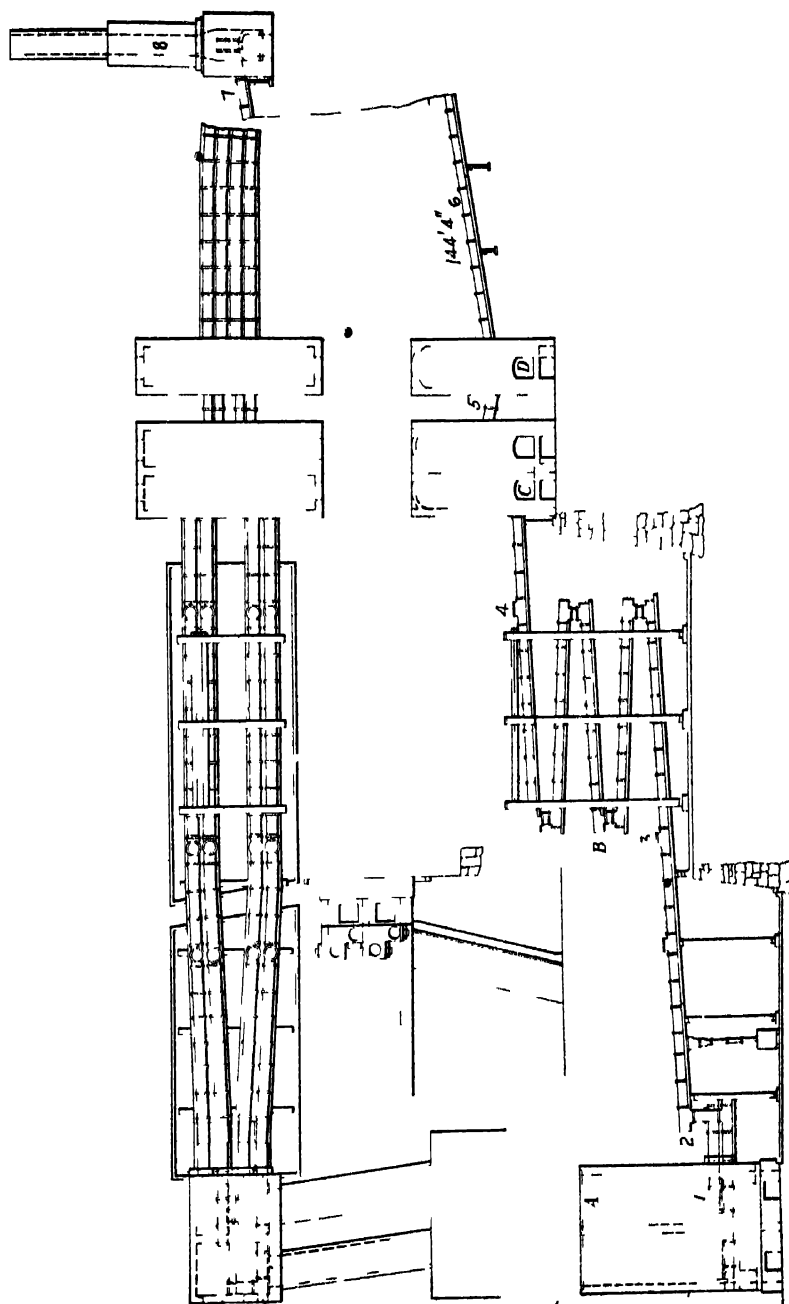


FIG 8—Tile pipe condenser at Oat Hill



pit" to the brick chimneys. When particularly wet ore is being charged, a booster fire can be built in the "rear ash pit" to increase the heat of the dryer gases.

**The Condenser System.**—The areas, volumes, and materials of construction of the various units of the condenser system are given in Table 1. The condenser system operates on natural draft. Provision has been made in the stack for aiding the draft by heating the stack gases, but this is very rarely necessary.

The furnace gases pass from the exit pipe into the first two chambers of the brick condenser, from here they pass to the second chamber through an opening in the bottom of the dividing wall, and from this second chamber the gases pass into the tile pipes to the cooling unit.

The gases of each exit pipe are kept apart in the first brick condenser by a central dividing wall, so that by closing off one exit pipe with the shutters provided for that purpose the corresponding half of the condenser is isolated, and the sheet-iron top can be removed for cleaning or repairs.

Sheet-iron slides are placed in the tile-pipe strings where they leave the brick condenser so that each string can be shut off for repair or cleaning.

TABLE 1 CONDENSER SYSTEM DATA

Part of system	Area, square feet	Volume, cubic feet
Two iron-topped brick exit pipes, 2 ft 9 in by 2 ft 6 in by 16 ft	536	220
One four-compartment non-topped brick condenser each compartment 4 ft 11 in by 3 ft 4 in by 18 ft	1,319	1,180
Four tile-pipe strings, each 1 ft in diameter and 151 ft long	1,897	474
One four-compartment brick chamber, each compartment 3 ft 3 in by 8 ft 4 in by 12 ft	1,329	1,300
Four tile-pipe strings, each 1 ft in diameter and 2 ft 6 in long	31	8
Brick chamber, 3 ft 6 in by 17 ft 6 in by 12 ft	627	735
Four tile-pipe strings, each 1 ft in diameter and 144 ft 4 in long	1,814	453
Brick stack, 2 ft 4 in by 2 ft 4 in by 25 ft	233	136
Total	7,786	4,506

The tile-pipe strings are offset after leaving the brick condenser for purposes of cleaning. A drain is placed in each, part way between the brick condenser and the cooling unit.

**The Cooling Unit.**—The cooling unit consists of five superposed lines of tile pipe, each 20 ft long, and is arranged in two sections of two strings each, so that the pipes are accessible for repair, and in order to simplify the cooling-water distribution.

The cooling water is piped into launders placed centrally over each section of two strings. This launder has lips, reaching to the center lines of the tile-pipe strings. The water flows over these lips through holes bored into the side of the launder at the lip level. The water flow is controlled by wooden pegs in these holes.

The water, after flowing successively over the five pipe strings, drops to the concrete floor on which the entire condenser system is built, and, after passing through settling boxes, flows to waste.



FIG. 9.—Furnace and dryer under construction.

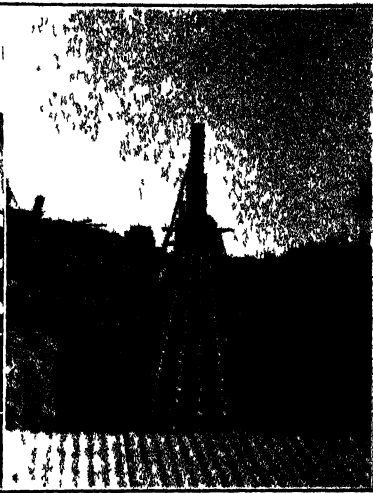


FIG. 10.—Stack and flue.

From the cooling unit the gases pass into brick chambers where any further dust and soot can settle, and from these chambers the gas passes to the stack through four tile-pipe flues

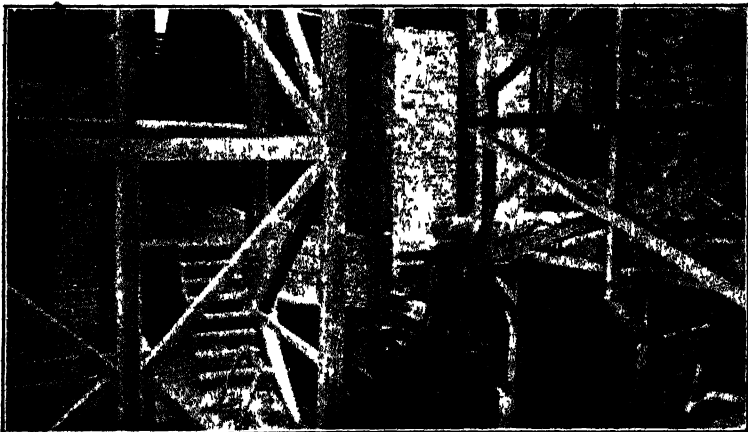


FIG. 11.—Details of plant showing furnace, exit pipes, brick condenser, tile pipes.

**The Stack.**—When it becomes necessary to aid the draft, a small fire is built in the fire box under the stack. The hot gases from the fire box pass through a small chimney into the stack proper, in this manner not only increasing the draft by heating the condenser gases but also by inducing a suction on the aspiration

principle. The design of this draft-inducing fire box is due to the suggestion of Dr. L. H. Duschak.

**Operation of the Furnace and Drier.**—The furnace treats about 40 tons of ore per 24 hr., with a fuel consumption of 2 cords of wood, the ore being crushed to 2 in. The wood for fuel—fir, manzanita, and oak—is obtained locally and as used contains about 11 per cent moisture.

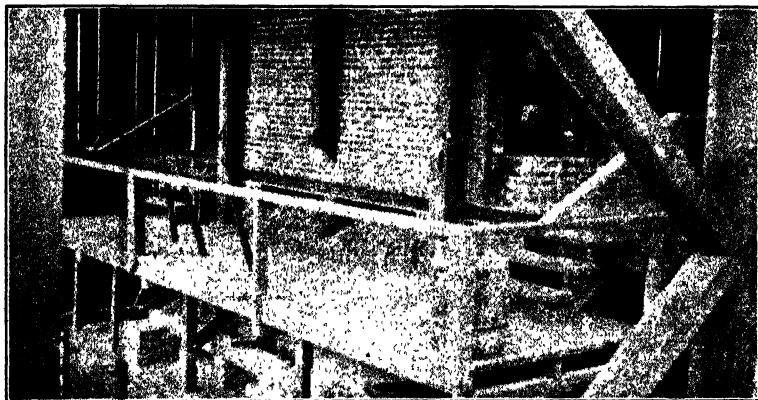


FIG. 12.—Dryer and furnace throat.

The ore is a sandstone, assaying between 5 and 6 lb. mercury per ton, the moisture content being around 8 to 9 per cent.

The furnace crew consists of one man per shift, who charges, draws, and fires the furnace.

All ore charged to the furnace passes through the drier. Soot from the clean-ups is charged into the furnace throat. The ore passes through the drier in 2 to 2½ hr. and in this time can be dried to a moisture content of less than one-half of 1 per cent.

One test showed a reduction of the moisture content from 8.5 to 0.28 per cent in 2 hr. A small booster fire was maintained during this test, the hot air entering the dryer at the rate of 1,200 cu. ft. per minute at a temperature of 260°C., and leaving the drier at a temperature of 120°C.

The temperature of the drying air is kept below 250°C., and is controlled by thermometers placed in the tops of the brick chimneys. The ore contains no native mercury, and as the vapor pressure of cinnabar is practically zero up to about 300°C.,<sup>1</sup> a loss of mercury in the drier is not probable. As stated above, the soot is charged into the furnace throat directly.

The drier increases the capacity of the furnace, and eliminates the possibility of a hang-up of the furnace, with its attendant danger of salivating the crew. Any hang-ups in the drier can be easily handled, as the drier flues are readily accessible through the peepholes provided for that purpose, and the work can be done without danger of salivation.

**Operation of the Condenser System.**—The condenser system operates on natural draft, the draft, of course, varying with barometric pressure and wind conditions. On sultry days the system is under a slight pressure, which can be

<sup>1</sup> Data taken from an unpublished thesis by Mr. Innes on "The Determination of the Vapor Pressure of Cinnabar"

relieved by a small fire in the stack fire box On clear, breezy days the draft is inward all along the system

In collecting temperature data, representative points along the condenser system were chosen, and all temperature readings were made at these points The distance that the gas has traveled at the various points of observation is given below

STATION	GAS TRAVEL IN FEET	STATION	GAS TRAVEL IN FEET
1	10	5	203
2	40	10	207
3	66	6	218
B	112	7	350
t	176	8	359
C	187	Top of stack	377

The following series of temperature readings were taken on the days following a clean-up The temperatures at corresponding points in the four parallel strings of tile pipe were found to be very nearly the same, so that temperature readings along one string were representative of the conditions obtaining in all four

TEMPERATURE TRAVEL  
(Last string)

Station	Feb 24 1919		Feb 25 1919		Feb 25 1919		Feb 26 1919	
	Time	Temperature degrees Centigrade	Time	Temperature degrees Centigrade	Time	Temperature degrees Centigrade	Time	Temperature degrees Centigrade
1	3 05	158	8 01	133	2 04	139	1 11	100
2	3 10	64	8 07	61	2 06	68	1 17	58
3	3 13	59	8 09	67	2 09	63	1 22	57
4	3 16	33	8 12	41	2 11	33	1 23	32
5	3 20	23	8 13	31	2 13	31	1 27	30
6	3 24	24	8 25	6	2 13	28	1 29	26
7	3 28	22	8 27	7	2 18	13	1 31	14
8	3 30	20	8 29	11	2 20	13	1 33	10
Atmosphere		11		7				8

Remarks Feb 24 sun shining Feb 25 cloudy no wind draft flue downcast Feb 25 cloudy windy Feb 26 sunny breezy draft in

The above-noted condition in one of the four flues leading to the stack (flue acting as a downcast) was also noted, on a few occasions, in the cooling unit

The table below was compiled from the record of daily temperature observations as made by the furnace foreman at the plant The temperatures recorded for the drier were taken at the top of the brick chimneys All temperatures were measured with thermometers.

**DAILY TEMPERATURE TRAVERSE, OAT HILL MINE, FEBRUARY, 1919**  
(Temperatures in degrees Centigrade at stations)

Date	1	A	2	B	C	D	7	Atmosphere	Drier
Feb. 1 .	154	120	60	44	30	27	17	8	82
Feb. 2 .	152	120	63	53	35	27	23	6	78
Feb. 3 . . . . .	153	120	62	49	30	27	17	7	76
Feb. 4 . . . . .	148	120	70		30	22	16	5	190
Feb. 5 . . . . .	152	120	53	34	32	32	18	..	190
Feb. 6 . . . . .	150	120	56	42	24	26	12	8	200
Feb. 7 . . . . .	160	126	60	48	32	26	17	10	230
Feb. 8 . . . . .	164	130	62	44	33	27	11	12	200
Feb. 9 . . . . .	166	134	62	44	23	21	11	10	218
Feb. 10 . . . . .	169	136	48	38	21	14	10	10	200
Feb. 11 . . . . .	163	128	50	36	19	18	6	4	198
Feb. 12 . . . . .	166	130	50	36	20	16	10	9	200
Feb. 13 . . . . .	167	136	56	36	21	20	9	6	210
Feb. 14 . . . . .	164	130	50	34	22	21	11	7	204
Feb. 15 . . . . .	164	134	59	32	22	20	10	6	210
Feb. 16 . . . . .	150	126	60	47	24	21	11	10	210
Feb. 17 . . . . .	158		60	40	23	22	12		215
Feb. 18 . . . . .	174	136	60	50	28	24			230

**The Cooling Unit.**—The following data on the performance of the cooling unit were taken just before the clean-up under the most unfavorable conditions for effective cooling, as the pipes were well coated with soot and mercury. The amounts at water were varied as shown in the table. The temperature readings were taken at stations 3 and 4 in the two outside strings of pipe. The flow of water as recorded is the amount for one section of two strings. A flow of 9 l. per minute is sufficient to keep a film of water on two strings of pipe.

**COOLING UNIT DATA, FEB 20, 1919**

Time	Temperature, degrees Centigrade			Water, liters per minute	Temperature, degrees Centigrade			Water, liters per minute	Remarks
	Station 3	Station 4	Difference		Station 3	Station 4	Difference		
2 45	74	50	24	0	66	46	20	0	After draw
3 05	75	50	25	0	63	41	22	10 8	
3 15	74	51	23	0	60	37	23	9 0	
3 25	74	50	24	0	59	35	24	9 0	
3 35	86	54	32	9	65	39	26	9 0	Draw
3 45	79	50	29	9	65	39	26	9 0	
3 55	77	45	32	9	64	37	27	9 0	
4 15	76	40	36	13 5	60	35	25	13 5	

TABLE 2.—STACK-FUME-LOSS DETERMINATIONS, SCOTT FURNACE, OAT HILL, 1919

Date 1919	Average temperature of flue gases degrees Centigrade	Barometric pressure stack millimeters of Hg	Fume sample		Velocity determination			Flue-gas volume				H <sub>g</sub> per cubic meter of dry gas 0°C 760 mm grams	H <sub>g</sub> vapor not re-covered in sample kilograms	Observed H <sub>g</sub> loss per 24 hr	
			Volume dry at 0°C 760 mm liters	H <sub>g</sub> found grams	Time noted seconds	Mean velocity		Discharge per minute stack condition	Discharge per 24 hr dry 0°C 760 mm cubic meters	Cubic feet	Cubic meters			Kilo-grams	Pounds
						Meters per second	Feet per second								
Feb 11	13.3	703.58	160.0	0.0027	29.0	1.08	3.54	660	18.6	23.600	0.0169	0.139	0.538	1.18	
Feb 12	11.3	718.56	204.0	0.0039	33.5	0.93	3.06	570	16.1	20.700	0.0191	0.147	0.543	1.19	
Feb 13	11.1	719.33	76.0	0.0030	36.0	0.87	2.85	530	15.0	19.300	0.0395	0.116	0.879	1.93	
Feb 14	9.5	714.47	69.5	0.0026	27.0	1.16	3.81	680	19.3	24.900	0.0374	0.124	1.055	2.32	
Feb 15	15.8	714.76	262.0	0.0080	31.0	1.01	3.31	600	17.0	21.200	0.0305	0.174	0.820	1.86	
Feb 17	12.3	713.99	104.0	0.0021	36.0	0.87	2.95	510	14.5	18.450	0.0202	0.125	0.497	1.09	

NOTE.—The velocity determinations were made over a distance of 114 ft.

During the above tests the following atmospheric temperatures obtained, for the first four readings, 13°C, for the next three readings, 12°C; and for the last one, 11°C.

**Gas Volume.**—The gas volume passing through the condenser system was calculated from the gas velocity as found over a distance of 114 ft in the stack flue between stations 6 and 7

The temperature of the gas and the barometric pressure at the time of the tests were recorded. The gas velocity was determined by the H<sub>2</sub>S method described in *Tech Paper 96*, U S Bureau of Mines. The mean velocity was assumed to be nine-tenths of the velocity as found.

The average of six gas-volume calculations gives a gas volume of 21,360 cu m of dry gas at 0°C and 760 mm per 24 hrs, or roughly 0.25 cu m per second.

The leakage of air into the condenser system varies with the natural-draft condition and was found to vary from zero to 10 per cent.

A series of stack-loss determinations were made and the data as found and calculated are given in Table 2.

While these determinations were made in winter under the most favorable conditions for effective condensation, the loss indicated is exceptionally low, and a large loss in the summer months is improbable if the cooling unit is liberally supplied with water.

**Clean-up of the Condenser System.**—The condenser system is cleaned at the end of each month. The free mercury and the soot are hoed out of the first brick condenser and carried to the soot pans. Then, successively one string of tile pipe is cut off by closing the shutter, and beginning at the top of the cooling unit the mercury and the soot are washed and hoed down progressively to the lower pipe, from where the material drops through the drains into the collecting boxes. From here the mercury and the soot are taken to the soot pans and worked in the usual manner. The brick chambers on the third terrace are only cleaned at long intervals, as very little mercury passes the cooling unit.

A fume sample of the gases taken at the point where they leave the cooling unit indicated a total mercury content of the gases passing this point in 24 hr of 3.68 lb. This result argues well for the condensing and baffling efficiency of the tile-pipe cooling unit.

There are no figures of recent date as to the cost of erecting a Scott furnace. Before the war, Scott himself estimated the cost of a 60-ton furnace, complete with brick condensers, at about \$60,000 or approximately \$1,000 per ton-day capacity.

The following is a list of materials required for a Scott furnace.

	10-ton	40-ton	50-ton
Common brick	150,000	300,000	400,000
Fire brick	12,000	20,000	30,000
Tiles	188	360	428
Cement (barrels)	25	40	50
Fire clay, timber for frame, iron for frame, grates, hopper, etc			

In all the early installations made by Scott, the thick brick-wall condenser was used. These brick condensers absorb a great deal of mercury, were hard to clean up, and in

the high temperature parts of the furnace and condensers wherever there is a dead space, due to a corner or lack of gas, the  $\text{SO}_2$  and volatilized mercury would unite to form a deposit of mercuric sulphate. This would not be possible in a condensing system such as the one described at the Oat Hill furnace, as there are no dead corners and the gases were always moving.

In all the early furnace installations in California wood was used as a fuel. In 1910 the New Idria mine, in San Benito County, California commenced using fuel oil, since which time many of the plants use this fuel. Fuel consumption varies greatly with the amount of sulphides in the ore (mostly iron pyrite).

At the New Idria mine the fuel consumption on the Scott furnace was about 10.3 gal of oil per ton of ore. (This was a residuum fuel oil 14 to 18°Bé.) At the Oceanic mine, in San Luis Obispo County, California, two 50-ton Scott furnaces used only 2 to 2½ cords of pine wood per day, on a comparatively heavy sulphide ore. At the Oat Hill mine, the 40-ton Scott furnace consumed about 2 cords of wood per day. In some California mines where Scott furnaces were used on heavy sulphide ore or sulphur ore, notably at the Corona, Helen, and Sulphur Bank mines, very little fuel was used, the ore being at times almost self-roasting.

During the war period, the U. S. Bureau of Mines, under the direction of Dr. L. H. Duschak, made an exhaustive investigation of quicksilver-furnace practice in California, particularly at the New Idria mine, in San Benito County, California, and the Oceanic mine, in San Luis Obispo County—the two largest producers of quicksilver in California at that time.

At the New Idria mine, there was one 75-ton Scott furnace and two 80-ton coarse-ore shaft furnaces, at the Oceanic, two 50-ton Scott furnaces. These tests proved conclusively that the stack losses from the Scott furnace were very small, a point on which operators up to that time were not sure. Exhaustive tests taken over a period of many months at both mines disclosed the fact that stack losses hardly, if ever, assumed a total loss of more than 2 per cent of the metal content of the ore. At New Idria on 0.7 per cent ore, the loss was but 4½ lb of quicksilver per 24 hr, treating 75 tons of ore. At the Oceanic mine on 0.3 per cent ore, it was 6½ lb, treating 90 tons. While top, stack, and discharge losses are controllable to a greater or less extent, there is one form of loss—that of absorption—that was practically impossible to measure and impossible to control where the old brick or stone condensers were used. The extent of this loss was proved at the New Idria and New Almadén plants when the condensers were taken down and quicksilver was followed down into the ground underneath them for a depth of 50 or 60 ft. This loss would be entirely obviated with the tile condenser system as described at the Oat Hill plant.

The work of the Bureau of Mines on quicksilver was described in an article by Dr. L. H. Duschak and C. N. Schuette on 'Fume and Other Losses in Condensing Quicksilver from Furnace Gases,'<sup>1</sup> from which the following is taken.

The work covered by this report was conducted by the Federal Bureau of Mines, through its experiment station at Berkeley, Cal., in cooperation with the New Idria Quicksilver Mining Company and the Oceanic quicksilver mine. Part of the expense was borne by these concerns and their liberality in placing their plant facilities at the disposal of the Bureau of Mines has greatly assisted the work.

The magnitude of the metal losses incident to the condensation of mercury from furnace gases has been a much-discussed question among quicksilver operators, but aside from the work of Christy<sup>2</sup> at New Almaden, Cal., in 1885 no study of the subject has been reported in this country. An elaborate examination of this question at the

<sup>1</sup> U. S. Bureau of Mines, *Techn. Paper* 96.

<sup>2</sup> CHRISTY, S. B. 'Quicksilver Condensation at New Almaden, Cal.,' *Trans. A. I. M. E.*, 14 (1885), 206.



Imperial Quicksilver Works at Idria (Krain, Austria) has been made by Castek.<sup>1</sup> No satisfactory application of his conclusions, however, can be made to American practice, because of the many ways in which this differs from European practice. Metal losses, amounting to 30 to 40 per cent of the plant input, have been suspected at some plants. Unfortunately, the conspicuous lack of technical control at quicksilver-reducing plants has usually rendered impossible the placing of even an upper limit for condenser losses by calculating the gross loss incident to the entire process of ore treatment.

The investigation described herein was undertaken with a view to making direct quantitative determinations of these losses.

**New Idria Quicksilver Mining Co.**—As more than two-thirds of the plant output of the New Idria company is derived from the No. 1 furnace, this was selected for study. It is a Huttner-Scott furnace (now commonly known as the Scott furnace), with rated capacity of 60 tons daily. In May, 1918, about 70 tons of fine ore and concentrate, making a charge averaging about 1.25 per cent mercury, was being treated in 24 hr.

Fuel oil of 18°Bé. gravity is used as fuel, there being two burners in the main fire box and one burner in the lower (rear) dust or vapor chamber. The fuel consumption per 24 hr. is about 450 gal., or 2.6 per cent by weight of the charge.

What is herein designated as the "old" condenser system comprised the customary series of brick and stone chambers followed by eight wooden barrels, then a blower, and a side-hill flue leading to the stack.

Before the second series of condenser-loss determinations was made, a "new" system was constructed, which retains only the first brick condenser of the "old" system. This condenser is followed by a line of tile pipe, then three large wooden tanks in series connected with wooden flues, followed by the eight wooden barrels, fan, flue, and stack of the former system.

**Oceanic Quicksilver Mining Co.**—Two Scott furnaces, with a rated capacity of 50 tons each, are in use at the Oceanic plant. About 90 tons of ore, carrying 0.25 to 0.3 per cent mercury, are treated in 24 hr.

Wood fuel is used in the main fire box only, there being no booster fire in the rear chamber. The total fuel consumption is 2 to 2.5 cords a day, or, roughly, 3 per cent by weight of the furnace charge.

Back of each furnace is a brick condenser, then a series of brick and wooden chambers, which combine into a common system leading to a side-hill flue and stack.

**Losses in Condensing Quicksilver.**—A preliminary survey showed that the usual methods of fume sampling employed at lead and copper smelters could not be used without considerable modification because of the large amount of water mist present in the stack gases. The method here described was developed and first used at the New Idria plant in May, 1917.

The gas passed successively through a glass sampling tube, a short Liebig condenser, a water-cooled bead tower, a Hawley filter,<sup>2</sup> and a wash bottle, and then through a small gas meter to a water jet pump, which provided the necessary suction.

The sampling tube was of glass, about 4 mm. (0.15 in.) in inner diameter, closed at one end but having, close to that end, an opening blown in the side. This tube

<sup>1</sup> CASTEK, FRANK, "Die Bestimmung und Verminderung der Verluste beim Quecksilberhüttenwesen," *Ber. Hüttenm. Jahrb.*, 58 (1910), 1 and 231.

<sup>2</sup> HAWLEY, F. G., "Determination of SO<sub>2</sub> in Flue Gas," *Eng. Min. J.*, 94 (1912), 987.

was placed with the opening near the middle of the gas stream and facing the direction of flow.

The bead tower which followed the Liebig condenser was of glass about 25 mm. (1 in.) in inner diameter, and 300 mm (12 in.) long. The upper two-thirds was filled with solid glass beads supported on a perforated porcelain plate. It is important that this plate be notched at the edges so that liquid collecting on the beads will not be prevented, by the ascending gas stream, from draining into the reservoir below. Both the Liebig condenser and the water jacket to the bead tower were cooled with ice water or cold tap water.

The Hawley filter was arranged in the usual way with accurately ground funnels about 90 mm (3.5 in.) in diameter. Soft, rather thick, filter paper was used. A section of the inner tube of a small automobile tire, placed with the smooth surface next to the glass, gave a firm and air-tight joint.

The wash bottle was charged with sodium hydroxide solution to remove  $\text{SO}_2$  before the gas passed to the meter. Considerable  $\text{CO}_2$  was no doubt absorbed also. A vertical water manometer interposed between the wash bottle and the gas meter indicated the reduction in pressure below atmospheric at which the meter worked.

In order to insure a steady and easily adjusted suction, a regulating device was placed in the circuit between the gas meter and the aspirator. This device consisted of a tall, glass cylinder with a two-hole stopper, a movable glass tube for admitting air passed through one hole and the other carried a T-tube through which the meter and the aspirator were connected.

Thermometers were placed in the water jacket of the bead tower, the gas meter, and in the stack carrying the gases under examination.

At each plant a sampling point in the flue system was selected, beyond which the amount of mercury recovered was negligible. At the New Idria plant samples were drawn from the 35-ft. wooden stack, a few feet above its base.

At the Oceanic plant an auxiliary draft flue carrying hot gases from a wood fire enters the main 3-ft. flue a short distance from the stack. Samples were, therefore, taken from the main flue just before the juncture with the auxiliary draft flues.

**Sampling Procedure.**—After the apparatus, except the sampling tube, had been assembled, the aspirator was started and, by closing the intake end of the system, a test was made to ascertain that the system did not leak. Special care in placing the sampling tube in the stack or flue was necessary in order to avoid contamination by the mercury that coated the interior. Error from this source was avoided by wrapping the sampling tube in a strip of paper twisted together at the end. The paper-covered tube was shoved part way into the stack or flue and the sampling tube was then punched through the twisted end. In removing the sampling tube the operation was reversed, the tube was drawn well into the paper cover, then the tube and the paper were withdrawn together. After the sampling tube had been properly connected, the meter was set at zero and the taking of the sample started by closing a by-pass connected to the suction line from the aspirator.

The suction was so regulated that gas was drawn through the apparatus at the rate of approximately 2 l per minute. At this rate the velocity of the gas entering the sampling tube was roughly that of the gas stream. In spite of the precautions for stopping the water vapor and mist, the filter paper gradually became damp, thus considerably increasing the resistance offered to the passage of gas. The effect of this higher resistance was, in a measure, offset by increasing the suction, which, however, was limited by the inability of the moist filter paper to withstand a pressure of more

than 100 to 180 mm. of water. Therefore, the rate of sampling decreased gradually, but, in view of the low velocity of the flue gases (less than 2 m. per second) and the minuteness of the fume particles in suspension, it seems unlikely that the momentum of any appreciable number of particles was sufficient to cause them to enter the sampling tube except with the gas stream. Difficulty from dampening of the filter paper was least when ice water was used in the condenser and in the jacket of the bead tower.

At intervals during the sampling period the flue gas, meter, and water-jacket temperatures and the meter and water manometer readings were recorded. Also, the barometric pressure was noted, and usually at least one flue-gas velocity determination was made by the method described in a subsequent page. Sample taking usually continued until several hundred liters of gas had been withdrawn, or until the rate fell off considerably.

The efficiency of the condensing and filtering apparatus in collecting the mercury was tested by placing a second bead tower and Hawley filter just after the first set in one of the tests. The mercury recovered from the two units was as follows: first tower and filter, 0.0199 g.; second tower and filter, 0.0007 g. Evidently not more than a few per cent of mercury mist in the fume samples escaped recovery.



FIG. 13.—Tilt-pipe cooling unit.



FIG. 14.—Fume sampling apparatus at stack.

**Preparation and Analysis of Sample.**—At the close of an experiment, the sampling tube, condenser tube, bead tower, and other parts of the apparatus, including the rubber connections, which might have collected any mercury, were carefully washed with nitric acid. Great care was exercised to avoid any “salting” of the sample by mercury-bearing dirt. This precaution was particularly necessary with the sampling tube, which was thoroughly cleaned on the outside before the mercury within was dissolved.

The glass beads were cleaned by stirring them in a beaker with hot dilute nitric acid and subsequently washing them in a funnel. This procedure was repeated at least once.

All nitric-acid solutions that might contain mercury were collected and brought nearly to the neutral point with ammonium hydroxide. Hydrogen sulphide was then passed in for some time, the precipitate was collected on a filter, and the filtrate was again treated with hydrogen sulphide to insure complete precipitation. Any mercuric sulphide in the fume sample obviously would not be affected by the nitric acid treatment, but as the solution was not filtered before precipitation with  $H_2S$ , this sulphide would be collected with the precipitated sulphide.

This filter paper bearing the mercuric sulphide precipitate and the paper from the Hawley filter constituted the sample; this was analyzed by a method developed for the purpose.

**Flue-gas Volume Determination.**—The low velocity of the flue gases—less than 2 m. per second—rendered the use of a Pitot tube impossible. Attempts were made to determine the velocity by shooting a cloud of colored dust into the gas stream but, presumably because of the large amount of water mist in suspension, the effect at the stack was too slight to be determined with certainty. The problem was successfully solved by injecting 10 to 12 l of hydrogen sulphide ( $H_2S$ ) at the lower end of the flue and detecting, by chemical means, its appearance at the end of a measured length of flue.

A large rubber bag with a neck 2 cm. in diameter was placed between two boards, thus forming a sort of bellows with which the entire volume of hydrogen sulphide could be injected within a fraction of a second. A glass sampling tube with several openings was placed well across the flue and a stream of gas was drawn by the aspirator from this tube through a small gas-washing tube containing 1 or 2 cc. of lead acetate solution.<sup>1</sup> A fairly concentrated lead acetate solution slightly acidulated with nitric or acetic acid was found to be most sensitive. The timing was with a stop watch.

The observed velocity was assumed to be a maximum corresponding with that of the more rapidly moving central core of the gas stream. The mean velocity was computed by using the factor 0.9 based on Loeb's experiments. From the mean velocity so obtained, and the flue diameter, which was 3 ft. at each place, the gas volume was computed.

As a check on this method, the gas volume was calculated from the fuel consumption and the carbon dioxide content of the stack gases, which were carefully observed during a three-day period. This calculation showed a stack-gas volume of 75,800 cu. m. of dry gas at standard conditions per 24 hr. The average derived from three velocity determinations during this period was 72,300 cu. m. In view of the difficulties involved in determining flue-gas volumes, the agreement is considered satisfactory.

**Calculation of Results.**—In calculating the stack loss from the results of the fume sampling, the volume of dry gas at standard conditions was used as a basis. The observed volume of the sample, as indicated by the meter, was corrected for the meter temperature and for the partial pressure of the dry gas. This latter is equal to the reading of barometric pressure decreased by the aqueous tension at the meter temperature and by the reduced pressure under which the meter operated, as indicated by the manometer. A further correction, in the sense of increasing the sample volume by about 4 per cent, was necessary because of the carbon dioxide and sulphur dioxide absorbed by the wash bottle preceding the meter.

Similar corrections based on the mean flue temperature, the barometric pressure, and the tension of water vapor were applied to the flue-gas volume.

As the sampling procedure did not completely remove all mercury vapor from the flue gas, a correction based on the vapor tension of mercury at the mean temperature of the Liebig condenser and lead tower must be added to the figure for mercury recovered. The earlier values for the vapor tension of mercury below 100°C., includ-

<sup>1</sup> LOEB, E., "The Pitot Tube Applied to the Measurement of Air," *Jour. Am. Soc. Nav. Eng.*, **24** (November, 1912), 1115.

ing those of Regnault,<sup>1</sup> which have been used rather generally in metallurgical calculations, are much too high.

**Results.**—A summary of the fume-loss determinations is given in Table 3. The losses shown are to be taken as minimum rather than maximum, since such analytical and other errors as were present would be negative. The variation in individual results may only in part be charged to experimental error, because the furnace conditions, particularly at New Idria, where concentrate was charged at intervals, were not constant.

TABLE 3.—MERCURY LOSSES IN FLUE GAS AT NEW IDRIA AND AT OCEANIC

Item	New Idria		Oceanic
	Old system	New system	
Mean temperature, degrees Centigrade. . . . .	39.4	37.7	31.9
Observed loss per cubic meter of dry gas at standard conditions, grams . . . . .	0.0393	0.1145	0.0556
Volume of gas at standard conditions corresponding to 1 cu. m. of stack gas, cubic meter. . . . .	0.734	0.742	0.846
Total loss per cubic meter of stack gas, grams of Hg . . . . .	0.029	0.085	0.047
Vapor loss, grams of Hg. . . . .	0.059	0.052	0.034
Mist loss by difference, grams of Hg. . . . .	.....	0.033	0.013
Mist, per cent . . . . .	.....	39	28

According to these calculations the gas leaving the old condenser system at New Idria is only half saturated with mercury vapor. This result may seem somewhat surprising, but was presumably due to the large amount of air leaking into the condenser system at various points, and to the slow rate of evaporation of the mercury particles covered with a protecting water film. A similar unsaturated condition, as regards arsenic trioxide in the flue gas from a copper smelter, is noted in *Tech. Paper 81* of the Bureau of Mines.<sup>2</sup>

It is not at all certain that in the other instances the stack gas was saturated with mercury vapor, although enough metal for this purpose was present.

That the mercurial particles leaving the stack are largely free metal is indicated by the following analysis of sludge from the base of the stack. After separating, by centrifuging, as much free mercury and water as possible, the air-dried residue had the following composition:

## ANALYSIS OF RESIDUE

	PER CENT
Hg (metallic) . . . . .	64.3
HgS . . . . .	5.0
Mineral matter (non-volatile) . . . . .	4.2
Moisture, acid, and organic matter (by difference) . . . . .	26.5
Total . . . . .	100.0

<sup>1</sup> REGNAULT, "Forces elastiques des vapeurs a saturation dans le vide," *Mem. Acad. Sci. France*, 26, (1862), 339.

<sup>2</sup> WELCH, H. V., and DUSCHAK, L. H., "The Vapor Pressure of Arsenic Trioxide," Bureau of Mines, *Tech. Paper 81* (1915), 20.

**Comparison with Previous Results.**—Christy,<sup>1</sup> from a careful study of the operation of one of the fine-ore (*terra*) furnaces at New Almaden, which received 320.9 kg of mercury in the form of 1.51 per cent ore per 24 hr, accounted for the metal input as follows

DISTRIBUTION OF MERCURY IN TREATING ORE AT NEW ALMADEN, CAL.

	PER CENT
Direct yield	92.71
Residue loss	0.66
Vapor loss	1.73
Mist loss (by difference)	4.90
Total	100.00

Taking his figure for the gas volume leaving the stack at 20°C as 24,306 cu m per 24 hr., the above loss is equivalent to a mercury content of 0.656 g to the cubic meter. Of this content 0.232 g is charged to vapor loss through the use of an erroneous value for the vapor tension of mercury at this temperature. The correct value for the vapor loss is 0.0132 g to the cubic meter. No direct determinations of stack loss were made by Christy, and, as the values that he adopted were obtained by difference, it is likely that they include losses occurring in other ways. Inaccuracies in sampling and assaying would also affect his result.

Castek's<sup>2</sup> paper on losses at Idria, Austria, contains a tabulation of stack-loss determinations that indicate an average content of 0.00232 g of mercury per cubic meter of stack gas. With a gas volume of approximately 177,000 cu m (stack conditions 15°C and 724 mm) per 24 hr, the daily loss was, therefore, 411 g, which was about 0.03 per cent of the daily production. The above figure for the mercury content of the Idria stack gas is much less than the values given in Table 3. Apparently, however, the sampling procedure at Idria, which is briefly described as filtration of the stack gas through a plug of glass wool or asbestos in a glass tube, was designed to stop only the mercury mist.

Castek<sup>3</sup> says that a number of attempts to detect a vapor loss<sup>4</sup> gave uniformly negative results. Apparently, the stack gas was far from being saturated with mercury vapor. Castek, however, adopts the erroneous value used by Christy in calculating the vapor loss and thus arrives at a value about twenty-five times too large.

**Discussion.**—The stack losses that the authors found are very small and represent at the New Idria furnace less than 1 per cent and at the Oceanic less than 2 per cent of the mercury input, but it is instructive to determine whether the relative magnitude of these losses is in any way related to the form of condenser system in use. The old system at New Idria consisted of the conventional brick and stone chambers, followed by wooden barrels and a side-hill flue and stack. In the new system only the first brick condenser was retained. From this a tile pipe led to the first of a series of three wooden tanks of about 9,000 cu ft. capacity each. A stream of cold air equal to about one-third of the gas volume leaving the furnace was introduced into the tile pipe just beyond the first brick condenser. The 10-in. pipe carrying the air stream was introduced parallel to the center line of the tile pipe. A water spray was injected with the air.

<sup>1</sup> CHRISTY, S. B., "Quicksilver Condensation at New Almaden, Cal." *Trans. A. I. M. E.* **14** (1885), 206-265.

<sup>2</sup> CASTEK, FRANZ, "Die Bestimmung und Verminderung der Verluste beim Quecksilberhüttenwesen," *Berg und Hüttenm. Jahrb.*, **85** (1910) 235.

<sup>3</sup> CASTEK, FRANZ, *op. cit.*, 239.

The condenser system at Oceanic consists largely of rectangular wooden chambers. Such data pertaining to these condenser systems as may have a bearing on fume losses is assembled in Table 4.

TABLE 4.—DATA ON CONDENSER SYSTEMS

Item	New Idria		Oceanic	
	No. 1, old	No. 1, new	No. 1	No. 2
Interior volume, cubic meters	489 <sup>1</sup> 0	1,098 5	723.9	1,090 0
Interior area, square meters	1,331 8	1,651 5	1,555 2	1,505 9
Materials of construction, percentage of volume enclosed by.				
Iron and tile	1 00	1 20	0 80	0 60
Brick and stone	63 00	8 20	27 00	16 00
Wood	36 00	90 60	72 20	83 40
Length of gas path, meters	261 0	253 0	165 0	166 0
Changes of direction of gas stream	52	26	25	12
Changes of velocity of gas stream	48	24	30	10
Gas volume, cubic meters at stack conditions.				
Per 24 hr	69,800	97,430	62,800	
Per ton of ore <sup>1</sup>	1,160(60)	1,400(70)	700(90)	
Per kilogram of Hg <sup>1</sup>	116(600)	118(825)	370(170)	
Mean flue velocity, meters per second	1 37	1 91	1 23	
Mean stack temperature, degrees Centigrade	39 4	37 7	31 9	
Hg content per cubic meter of gas, stack conditions, grams	0 029	0 085	0 047	
Loss of Hg per 24 hr, kilograms	2 01	8 18	2 94	

<sup>1</sup> Figures in parenthesis indicate approximate daily quicksilver production in kilograms

As regards the old and the new systems at New Idria, the daily loss from the latter was roughly four times that from the former, although the volume of the new condenser system is more than double that of the old. On the other hand, the factors favoring a larger loss from the new system were a gas volume 50 per cent larger, with a consequently higher mean velocity throughout the condenser system, and fewer changes of velocity and direction in the gas stream. The final stack temperature was essentially the same in both systems.

Comparison of the old system at New Idria with the Oceanic system shows that the equivalent volume of the latter, which is composed of two partly separate systems, is about twice that of the former; also, the mean stack temperature at Oceanic is considerably lower. In spite of these favorable factors the daily mercury loss is a little larger. It is to be noted, however, that the number of changes in velocity and direction of the gas stream is distinctly less at Oceanic.

A permissible conclusion from the data just presented is that the baffling effect in the conventional brick or stone condenser system is considerably more effective in recovering quicksilver than is a mere increase in condenser volume.

It is obvious, of course, that the gas volume should be as small as possible. For a given condenser system, other things being constant, an increase in the gas volume will produce more than a proportionate increase in the mist loss alone, because the higher velocity of the gas stream will considerably increase its carrying power. Richards<sup>1</sup> says that the carrying power of the gas stream is probably proportional to the cube of its velocity. The vapor loss, assuming the stack gas to be saturated, would be proportional to the volume.

As regards vapor loss, a reduction to 20°C of the temperature of the gas leaving the new system at New Idria would convert nearly three-fourths of the escaping mercury vapor, equivalent to 3.6 kg (8 lb) per 24 hr, into mist which could be recovered if recovery were deemed worth while. A similar reduction in temperature at Oceanic would convert, roughly, three-fifths of the vapor equivalent to 1.2 kg (2.6 lb) per 24 hr, into mist.

The mercury particles in suspension, as has been suggested above, can be partly removed from the gas stream by suitable baffling. An elaborate series of experiments on the separation of suspended particles from the gas stream by different methods of baffling was conducted at the Great Falls plant of the Anaconda Copper Mining Company several years ago. From consideration of the amount of dust collected, the interference with draft, and other important factors, including the cost of construction, it was concluded that baffles consisting of wires hung vertically a few inches apart were the most effective.<sup>2</sup> In a quicksilver condenser vertical strips of wood might be used instead of wires.

Without doubt, the most effective way of recovering all mercury in suspension would be by electrical precipitation. This method has been employed by the New Almaden Quicksilver Mining Co., in connection with its Herreshoff furnaces, both for removing dust from the hot gases and for recovering mercury mist from the final stack gases.

The practicability of installing a system for recovering the mercury mist from the stack gases is a question which would require study at each plant. A more detailed consideration of this question and of the general condenser problem is reserved for a later paper.

**Water Losses.**—Water escaping from a condenser system may carry mercury either in the form of minute metallic particles, commonly called flowered mercury, or in the form of mercury salts in solution. Castek<sup>3</sup> concluded that at Idria the mercury loss in the water leaving the first portion of the condenser system, which was constructed of vitrified stoneware pipes, amounted to about 0.1 per cent of the input, or, roughly, 17 kg a day.

The question of water losses was investigated coincident with the determination of stack loss. With the old condenser system at New Idria it was impossible to measure or to sample accurately the water leaving the condenser system, as an unknown amount escaped through the bottom of the brick and stone condensers into the earth. A sample of water taken shortly after a clean-up and probably carrying more than the normal amount of mercury was found to contain 0.15 g of mercury per liter. In the absence of a direct determination, the maximum amount of water that might escape from the condenser system was calculated by deducting from the total amount leaving the furnace the part escaping from the stack as mist and water vapor. This latter figure was arrived at from some rough observations taken in the

<sup>1</sup> RICHARDS, J. W. 'Metallurgical Calculations,' part 3, pp. 630-631, 1908.

<sup>2</sup> GOODALE, C. W. and KLEPINGER, J. H. 'The Great Falls Flue System and Chimney,' *Trans. A. I. M. E.*, **46** (1913), 593.

<sup>3</sup> CASTEK, FRANZ. "Die Bestimmung und Verminderung der Verluste beim Quecksilberhüttenwesen," *Berg und Hüttenm. Jahrb.*, **88** (1910), 231.



course of the fume sampling. On that basis the waste water was found to be something less than 2,000 l. a day. If this is taken as an average value, the corresponding mercury loss is 0.3 kg. (0.66 lb.) a day, or 0.05 per cent of the furnace output.

In operating the new condenser system, water was sprayed into the gas stream and also applied at a number of points to the outside of the wooden tanks and pipe connections. This cooling water, with the water condensed from the furnace gases, escaped from the system at two points. The water from the first and second wooden condensers flowed through a series of launders to a single wooden settling box and thence to waste; that from the rest of the system passed through a long series of launders and then through several settling boxes. A number of measurements were made of the volume of water leaving each section of the condenser system under varying conditions, and average samples were taken from each water stream at the point where it finally ran to waste. The results of these observations are given in Table 5.

TABLE 5.—WATER-LOSS DATA, NEW CONDENSER SYSTEM, NEW IDRIA

	Conditions	First section, tanks 1 and 2	Second section, tanks 3, etc.
Mercury in solution, grams per liter . .	Normal	0.0404	Trace
Mercury in suspension, grams per liter. . .	Normal	0.0412	0.0056
Mercury in solution, grams per liter . . .	Just after run down	0.0088	
Mercury in suspension, grams per liter.	Just after run down	0.1395	
Volume of water per 24 hr., liters. . . . .	Normal	26,300	8,770
Volume of water per 24 hr., liters. . . . .	Maximum	40,900	29,650
Mercury lost per 24 hr., kilograms. . . . .	Normal	2.14	0.049

The so-called normal loss was thus 2.14 kg. of mercury per 24 hr. To this must be added about 0.5 kg., representing the additional daily loss occasioned by the agitation of the daily run down. This leads to a total loss of 2.64 kg. (5.8 lb.) a day. The corresponding loss for the maximum water volume observed would be about one and one-half times this.

At the Oceanic plant all condenser water went to a single settling tank. A sample of the overflow from this tank was found to contain 0.018 g. of mercury per liter. With an estimated daily flow of 1,500 l., the mercury loss would be 0.027 kg. (0.06 lb.).

The relatively large loss in the new system at New Idria may be attributed primarily to the increased quantity of water which was, roughly, twenty times that in either of the other systems. Under normal conditions about 50 per cent of this loss was due to metal in suspension, and during the period of the run-down the mercury escaping was largely in this form. No doubt a considerable proportion of this suspended metal could be recovered in a suitable system of settling tanks.

The mercury in solution was probably present as sulphate, resulting from the action of sulphuric acid on the metal. Mercury can be completely precipitated from solution by scrap iron, but if the condenser water contains much acid, the consumption of iron might be out of proportion to the mercury recovered. At New Idria it so happened that the water supplied to the condensers contains alkali enough to neutral-

use the acid from the furnace, so that sometimes the water leaving the condenser system was actually alkaline. Under these conditions the wastage of iron should be small.

**Other Sources of Loss.**—Although the loss of metal is not susceptible of measurement, certain other ways in which mercury may escape from the condenser system deserve mention.

It is the usual practice both in this country and in Europe to avoid the danger of mercury loss through gas leakage by operating the condenser system under a slightly reduced draft. There can be little question as to the wisdom of this procedure, for a slight escape of mercury-laden gas will result in a vastly greater loss than that occasioned by the inward leakage of a like amount of air. For example, the daily leakage of 2,500 cu. m. of saturated gas, at 100°C., would result in a vapor loss of 8.1 kg. (17.8 lb.), and the actual loss would probably be somewhat greater because of mercury particles in suspension. This volume is less than 5 per cent of the gas flow observed at the Oceanic plant.

As an inward leakage of air amounting to 20 to 50 per cent of the gas stream has been observed at several furnaces, it is evident that a large loss would result from an equal outward leakage. The danger of serious loss is greatest close to the furnace where the temperature is high and the mercury content of the gases large. The pressure at the top of any condensing chamber will be greater than at the bottom, and for the taller parts of the condenser system, particularly those near the furnace, there may be a considerable pressure difference. An inward draft at the bottom does not necessarily mean an inward draft at the top. Moreover, owing to the more vigorous air currents near the top of the condenser system, leaks in that region may not be evident. All parts of a condenser system should be readily accessible for inspection, and inclined draft gages, such as the Ellison gage, may be used at danger points with advantage, to indicate whether a safe condition of inward draft is being maintained.

**Absorption Losses.**—Under absorption losses are included those losses arising from the penetration of the condenser material by mercury. As has been pointed out by Castek<sup>1</sup> and others, this loss is most noticeable with a new condenser system and the mercury retained by the condenser material is supposed to be recovered eventually.

Mercury loss, however, can occur through the use of pervious condenser material in ways that do not appear to have been recognized. One of the authors of this paper has observed that when in the course of the periodic "clean-ups" the interior of the brick condensing chambers close to the furnace was washed with water a shower of mercury was apt to fall from the outer surface. This was presumably due to the expulsion of mercury contained in the pores of the brickwork by steam arising from the water that penetrated the hot condenser wall. A similar action may take place automatically at certain points through fluctuations in temperature and in moisture content of the furnace gases.

The phenomenon just cited supports the common belief that the brickwork of an old condenser system is pretty well saturated with mercury. When this condition exists, a considerable surface, in the aggregate, of mercury may be exposed on the exterior of the condenser system, and where the temperature is high it is not unlikely that considerable evaporation of mercury occurs. The possibilities in this direction are indicated by some calculations made from data presented by Knudsen.<sup>2</sup>

<sup>1</sup> CASTEK, FRANZ, *op cit*.

<sup>2</sup> KNUDSEN, MARTIN, "Die maximale Verdampfungsgeschwindigkeit des Quecksilbers," *Ann. Physik.*, 47 (1915), 667-708.

The amount of mercury that should theoretically evaporate in 24 hr. from 1 sq. m. of mercury surface in vacuum is, roughly, as follows: at 100°C., 10,000 kg.; at 50°C., 480 kg.; and at 30°C., 110 kg. This enormous rate of evaporation has been nearly attained in actual experiments in vacuum, but in the presence of other gases the rate would be very much less. Assuming that mercury exposed to air will evaporate at only one-thousandth of the above rate, the amount of metal which may be lost in 24 hr. per square meter of surface exposed is still large. Moreover, the appearance of some of the condenser systems now in use suggests that the aggregate mercury surface exposed may be considerable.

These considerations emphasize the desirability of building condensers of material impervious to mercury vapor.

**Mechanical Losses.**—Mechanical losses of mercury may occur through leaks in the bottom of a condenser system and through spattering during "clean-ups." The older practice of building condensers on or close to the ground makes proper inspection practically impossible, and the quantities of mercury that have recently been recovered from the ground below condenser foundations at two plants in California are convincing evidence that this source of loss should not be neglected.

The practice, now favored, of supporting condensers well above ground, with properly inclined concrete floors below, largely eliminates the danger of mechanical loss.

**Conclusions as to Condenser Losses.**—The condenser losses that can be accurately measured represent at most only a few per cent of the plant output. One should not conclude from this, however, that the overall efficiency of condensing systems now in use is of the order of 95 per cent. The losses mentioned above have undoubtedly been large at times. The point of fundamental importance established by this investigation is that there are no inherent difficulties that prevent the recovery of at least 96 to 99 per cent of the mercury vapor entering the condenser system.

**The Rotary Furnace.**—This furnace and condensing system was perfected during the war period (1917 to 1918) at the New Idria mine, in San Benito County, California, and at the Sulphur Bank mine in Lake County, California. Since the first furnace was completed in 1917, practically all new quicksilver furnace installations have been of this type and over three-quarters of all the tonnage of quicksilver ore in the United States is now burned in these rotaries.

The five-furnace plant built at the New Idria mine has the largest capacity of any quicksilver reduction plant in the world. The furnace is built to treat quicksilver ores of all kinds under any and all conditions, from wet ore, mud, or dust up to material that will pass through a 3-in. ring with no preliminary drying on wet ore.

Each furnace and condensing system is built as an individual installation and made to meet and conform with the requirements and peculiarities of each kind of ore to be treated.

A few of the many advantages claimed for these reduction plants are as follows: lower cost of installation and maintenance and fuel economy; an advantage claimed over the shelf furnace is that both charging and drawing are mechanical, eliminating the personal element; labor costs are very low and the work easier for the operator; no salivation of workmen, as there is no leakage of fumes; will give almost complete extraction on ore carrying free mercury and will roast effectively very fine ore or dust;

can be fired and running at capacity with oil or gas in less than 2 hr ; to shut down one simply shuts off the fire. Any large brick and tile furnace requires six to eighteen days' time to fire up and several days to close down.

A rotary of the latest type can be relined in a short time—one to four days, while a brick and tile furnace would require about three months to reline completely with new tile throughout.

There is no absorption of quicksilver in the furnace and very little in the condensing system—never over a few flasks and only a small fraction of what sometimes was tied up in the old-time brick condenser.

The condenser system is easily cleaned up. Much less labor is required and less chance of mercurial poisoning of the operators.

As the ore is roasted in a short time—30 to 60 min—it is always in motion and never inert, allowing the mercury fumes as soon as vaporized to be carried away to the condensers at once, obviating the possibility of the formation of mercurous sulphates, chlorides, etc.

The rotary furnace is a tube of the revolving cement-kiln type, arranged with the necessary sealed joints at each end, fire box, dust chamber, etc., to roast quicksilver ores.

They have been built so far in four sizes and of varying lengths as follows:

DIAMETER, FEET	LENGTH, FEET	CAPACITY, TONS
2	24.30	10 to 25
3	36.48	25 to 60
4	56.64	60 to 120
5	72.84	70 to 150

The character of the ore determines the length of the tube, also its inclination, which ranges from  $1\frac{1}{2}$  to  $1\frac{1}{2}$  in per ft, and the kind of condensing system necessary. A 4-ft furnace (inside diameter) 60 ft long is made of  $1\frac{1}{4}$ -in steel plate with a 6-ft taper end on the upper or feed end. It is flush riveted on the inside to facilitate lining and butt strapped on all longitudinal seams and reinforced with heavy  $\frac{1}{2}$ -in plate for a distance of 4 ft, where the riding rings and gear rings are placed. The kilns have two heavy riding rings of cast chrome-vanadium steel, placed about a quarter of the distance from each end and turn on roller trunnions mounted on cast-iron sole plates. The upper riding ring is fitted with thrust rollers to hold the tube in place.

Each furnace is fitted with rub-ring expansion joints on each end, at the fire box and where the tube projects (about 12 in.) into the dust chamber. The ore is fed into the tube a distance of 4 to 8 ft.

Several types of feeders are used depending on the kind of ore fed. If dust or mud, a screw feeder is sometimes used. On coarse, granular ore a reciprocating shaker feeder, commonly called a "grasshopper," is very effective.

On the small 2-ft. tube a shovel feeder has been developed that gives good results.

The tubes are lined with fire brick—cast in special sizes made to fit each diameter of the circle and ranging in thickness from  $4\frac{1}{2}$  to 6 in. These should be made of good-quality material, well glazed and hard burned.

The life of a tube lining depends on the hardness of the ore and will range from eighteen months to five years. Relining is a comparatively small job and entails only a short shut-down.

It is claimed that oil, gas, coal, or wood can be used as fuel. If wood or coal is used, a special fire box is constructed outside, the heat passing through an opening directly into the tube.

Fuel oil (residuum of 14 to 18°Bé), however, is used in California and a brick hood is built over the fire end of the furnace and the burner (generally a high-pressure type)

is passed through a small opening directly into the tube 3 or 4 ft. Compressed air, or sometimes steam at 30 to 50 lb. pressure, is used to atomize the oil. Sufficient air for combustion is admitted through a door, generally below and over the burned-ore bin, and carefully controlled.

The burned ore leaving the tube drops on a gentle slope into the burned-ore bin, which should be made large enough to hold at least two shifts' run.

The flow sheet of one of the furnaces is comparatively simple and on a 4-ft. installation, as at the Cloverdale mine, Sonoma County, California, is about as follows:

The ore coming from the mine is passed over a grizzly with the bars spaced  $2\frac{1}{2}$  in. apart, the oversize going through a jaw crusher and dropping into the ore bin. It is fed from the ore bin either with a Challenge feeder or by gravity to the shaker feeder directly into tube, through the dust chamber.

The tube (on an inclination of  $\frac{3}{4}$  in. to the foot) revolves at the rate of one revolution in 55 sec. The ore gradually works down the tube, cascading somewhat in the fashion of ore in a tube mill.

The flame from the burner passes down directly on the ore just before it leaves the tube, heating the ore and also the lining of the tube, which is always turning under the ore. As the ore is heated, the mercury fumes are liberated and carried up the tube by the draft, the excess heat drying and heating the incoming ore in the upper reaches of the tube.

From the tube the gases pass into a dust chamber of brick or reinforced concrete 6 ft. wide, 12 ft. high, and 20 ft. long. In this dust chamber all the heavy dust is dropped and can be cleaned out when necessary through doors at the bottom. At the far end of this dust chamber a tower rises 16 ft. high, through which the gases pass, and thence down on a 45-deg. slope through an 18-in. round boiler-plate exit pipe to the condenser system.

In this exit pipe are placed three or four high-pressure Cyclone water sprays, spraying in the direction of travel of the gas stream. These sprays knock down most of the remaining dust, which is collected in a concrete box at the bottom of the exit pipe.

This dust carries considerable quicksilver and is retorted or recharged in the furnace.

The concrete box into which the exit pipe enters is 24 ft. long, 2 ft. wide, and 3 ft. high, inside measurements, with reinforced-concrete walls 12 in. thick. It is divided into 4-ft. compartments. The first one, No. 1, mentioned above, receives the dust from the exit pipe; the next one, No. 2, is divided from the first by a low wall 12 in. high. From this compartment two 15-in. double-strength, highly glazed, vitrified, round tile pipes leave at an angle of 45 deg. These tile lines are 25 ft. long and lead up on a scaffold to a platform to another junction box made of 2-in. plank and lined with 6 in. of concrete. The gas stream passes up through these two pipes, thence back through two more to compartment No. 3 of the lower concrete box. This cycle is continued from three to five times, depending upon the character of the ore burned. There is generally about 300 ft. of glazed tile pipe used in a four-furnace condensing system. As the gases come down the last time into the concrete box they pass out through a short pipe line of the same character to a settling chamber. This settling chamber is made of 1 by 6 in. flooring, and is 6 or 8 ft. in each dimension in cross-section, and 20 to 40 ft. long, with the floor and roof at an angle of about 40 deg. to facilitate the clean-up as all quicksilver, and soot drops out through doors into a wooden or concrete launder and is carried to the general clean-up.

From this settling chamber the gases are carried by the same tile pipe to a stack. If the terrain is favorable, this stack can be situated at considerable elevation above the plant—100 to 150 ft.—in which case there will be sufficient natural draft to carry the gas stream through the plant. If this is not possible, it is necessary to install a

blower of the Root, or positive, type to aid the draft. In California plants though this is hardly ever found necessary. Draft regulation on these furnaces, or on any other, is a very important factor and very close consideration must be given to natural conditions before the plant is installed, especially if situated in a cañon or in any point subject to variable air currents. Whether with natural draft or with forced draft, a very careful control is necessary at all times.

Where a heavy sulphide ore is burned, it is generally advisable to introduce a considerable amount of free air at low pressure into the gas stream in the exit pipe leaving the dust chamber. This also aids the draft from the furnace if the same is necessary.

These furnaces can be arranged in many different ways with the dust chamber extending either to the right or left of the feed end of the furnace. The condensing system can lead away from the dust chamber in almost any direction, depending upon the location. It should be arranged in such a manner as to bring the clean-up as much as possible in one place. All clean-up should be made on concrete floors and all water from the condensing system and settling chamber, tile lines, etc., should be passed into settling tanks of ample capacity. The plant can be cleaned up once a week or once a month. If arranged in the proper manner, this clean-up can be made in a couple of hours by one operator. Generally, the soot and the quicksilver as taken from the condensers are mixed with lime and hoed. The residue can either be recharged in the furnace or burned in a retort.

In all installations to date, one operator on a shift is sufficient. All large installations, say four furnaces, can be handled with two or three men per shift.

**The Herreshoff Furnace.**—This is a circular, mechanically rabbled furnace of the MacDougall type. One of these furnaces has been in operation at the Senator mine of the New Almaden company since 1917. It is 14 ft. in diameter and has six hearths with air-cooled shaft and rabble arms. It has a capacity of 34 to 40 tons per day.

On account of the large amount of dust raised and thrown into the fume circulation as the ore is rabbled from hearth to hearth, it was found necessary to install a Cottrell dust precipitator between the furnace and condensing system.

Though roasting the ore satisfactorily, the high cost of maintenance and operating, the necessity of having electric power to operate the Cottrell dust precipitator, and the comparatively high fuel consumption—all militate against the general use of these furnaces.

In the reduction of low-grade quicksilver ores today in this country a furnace plant and condensing system should have these general specifications:

It should have large capacity with low fuel consumption and as near as possible perfect draft control. The labor required should be reduced to an absolute minimum—100 tons per day with one man per shift is possible.

The ore should be roasted as quickly as possible consistent with fuel economy and the mercury fumes carried out of the furnace into the condensing system under a moderately strong draft.

The condenser system should be arranged so that clean-up can be made in as small a space as possible to avoid spillage and unnecessary handling of soot and quicksilver. Soot and quicksilver should at all times be handled on concrete floors.

All tile lines, settling chambers, conduits, and launders should be well up off the ground and, if possible, over concrete floors, so if leaks develop they can be seen at once. All concrete work inside the condensing unit should be painted with a heavy gilsonite paint on the inside and with any good asphaltic-base paint on the outside. This precaution is particularly important if the ore is a heavy sulphide or carries free

sulphur enough to make much sulphuric acid. If arsenic or antimony is present in the ore, other complications may arise

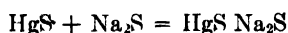
The entire system should be free from any leakage of fumes and, if from any cause there is leakage, the walls and the roof should be kept washed down to avoid chances of mercury poisoning of the operator.

**Concentration of Quicksilver Ore.**—While milling and concentration of quicksilver ores have been tried at several different mines in the country over a period of nearly twenty years, and though some of these efforts have been successful from a commercial standpoint—more particularly during the war and the period of high prices—nevertheless it can hardly be said that any plant has been a success as far as high extraction of the metal is concerned

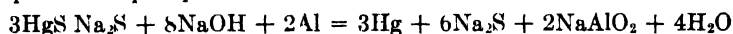
The first concentrating plant of any size of quicksilver ore was at the Manzanita mine, in Colusa County, California. From 1904 to 1912 this mine produced about 2,000 flasks of quicksilver, most of which was obtained by means of concentration. The ore was crushed in a 5-ft Huntington mill to 20 mesh and concentrated on six Gilpin County bumping tables, the tailings from which passed to cone classifiers, the overflow of which was passed over a belt vanner. The concentrates, averaging about 35 per cent Hg, were roasted in a Johnson-McKavert retort.

Later a similar plant was built at the Oat Hill, Napa County, and the Oceanic, San Luis Obispo County, mines. During the war period, with its stimulation of prices, considerable concentration was carried on in the state, notably at the New Idria, Oceanic, and Sulphur Bank mines. These plants were of 500, 300, and 500 tons daily capacity, respectively. As these plants have been described by Bradley in *Bull* 78, "Quicksilver Resources in California," no further description of them will be made here, and no further comment made on the concentration or flotation of quicksilver ores, except to say that only in isolated instances would concentration be successful. One reason for this is the fact that nearly anywhere in this country ore can be furnished cheaper than it can be ground and with an extraction of 95 per cent and better, while any milling and concentrating plant, followed by flotation, will not make over 80 or 85 per cent extraction, with the concentrates still to be roasted.

**Extraction of Mercury by Alkaline-sulphide Solutions.**—Though up to the present time no commercial plant has produced quicksilver from mine ores by this method, nevertheless it has possibilities. In 1915 a commercial plant of this type was operated at the Buffalo mine, Cobalt, Ont., and this is described by Thornhill.<sup>1</sup> The process developed at the Buffalo mine for this purpose consisted in leaching out the mercuric sulphide with a caustic alkaline sulphide solution, then precipitating the mercury from the solution with metallic aluminum. The equation for solution is



The equation for precipitation is



Small-scale experiments showed that a complete extraction of the mercuric sulphide could be made by an 8- to 10-min. treatment of the residue with the alkaline sulphide solution. H. G. S. Anderson, who was associated with Thornhill, made numerous experiments with this process on cinnabar ore with very good results.

During the war period several mines did experimental work with this process, but the most comprehensive work was done by W. W. Bradley, Assistant California State Mineralogist, on ores in different parts of the state.<sup>2</sup>

<sup>1</sup> A. I. M. E. *Bull* 104 1653-1657

<sup>2</sup> See "Quicksilver Resources of California," *Bull* 78

Generally speaking, the same objection, that is, the grinding of the ore, is applicable to this method as it is in wet concentration, as in nearly all instances it is cheaper to roast ore than it is to grind it.

**Quicksilver Assays.**—Assaying of quicksilver ores at the mines has never become general either in this country or in Europe. One reason for this is that the character of the ore in most mines is such as to make sampling very unreliable. Though the large mines of Spain and Italy all have well-equipped laboratories and competent metallurgists, no regular sampling and assaying is carried on.

In this country considerable assaying was done at the New Almaden mine in the eighties, but it was later discontinued. During the war period the New Idria mine, in San Benito County, assayed regularly for about two years. It was at this place and at the Sulphur Bank mine, in Lake County, that the assayers, working in conjunction with engineers from the U. S. Bureau of Mines, developed an improved quicksilver assay. It is essentially: distillation in an enclosed tube; then dissolving the mercury in concentrated  $\text{HNO}_3$  and titrating with thiocyanate. This method is considered the best as it is much quicker than the older methods and more reliable on high-grade ore, or where the ore contains much free sulphur, pyrites, and organic matter.

The method generally in use in this country, however, outside of the large mines, is what is called the Eschka, or Whutton, method in what is called the "Whutton quicksilver apparatus."<sup>1</sup>

<sup>1</sup> This method is fully described by W. W. BRADLEY, "Quicksilver Resources of California," *Bull.* 78, 282-283



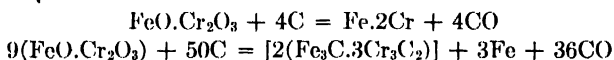
## CHAPTER XXXVI

### CHROMIUM

BY ROBERT M. KEENEY, E. MET.<sup>1</sup>

**Methods of Extraction.**—The requirements of modern industry have resulted in the development of three distinct metallurgical processes for the extraction of chromium from its mineral of commercial importance, chromite ( $\text{FeCr}_2\text{O}_4$ ), in forms suitable for steel manufacture, the dyeing and tanning industries, and for the production of special alloys of chromium free from iron having low electrical conductivity and great resistance to corrosion at high temperatures. These methods are: (1) the smelting of chromite in the electric furnace to produce ferrochromium; (2) the manufacture of chromates and bichromates by the chemical treatment of chromite; (3) the production of metallic chromium by chemical extraction of chromium oxide from chromite, followed by the reduction of the oxide to metal by the thermit process.

**Ferrochromium.**—The process of making ferrochromium<sup>2</sup> from chromite consists of mixing ore, coal, or coke, and, if necessary, lime, fluorspar, or quartz to form a suitable slag, and smelting the mixture in an electric furnace lined with magnesite. At about 2-hr. intervals the ferrochromium and slag are tapped into iron pots, the metal settling to the bottom. The pot is dumped when the contents have solidified. Reduction theoretically takes place according to the reactions:



These reactions represent two extremes, the first, the production of a carbon-free ferrochromium in a single operation, and the second, the production of an alloy with the maximum percentage of carbon, 10.4 per cent. In practice, the first reaction never takes place, and the latter seldom, so that the carbon content of ferrochromium produced from smelting chromite may vary from 4 to 8 per cent, depending somewhat on the grade of ore and the method of operation. Ferrochromium is, therefore, classified according to carbon content into the following grades: less than 1 per cent carbon, 1 to 2 per cent carbon, 4 to 6 per cent carbon, and 6 to 8 per cent carbon, the lower the carbon the higher the price of the alloy.

By smelting an ore containing 40 to 50 per cent  $\text{Cr}_2\text{O}_3$ , an alloy containing 60 to 70 per cent chromium is produced. The 4 to 6 per cent carbon grade and the 6 to 8 per cent carbon grade are the result of the initial smelting. The lower-carbon alloys are made by refining high-carbon ferrochromium with an oxidizing slag of chromite to remove the carbon. This operation must be conducted with great care and con-

<sup>1</sup> Industrial Heating Engineer, Connecticut Lt. & Power Co., Waterbury, Conn.

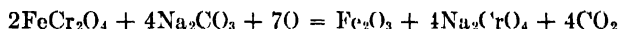
<sup>2</sup> LYON, D. A., KEENEY, R. M., CULLEN, J. F., "The Electric Furnace in Metallurgical Work," U. S. Bur. Mines, *Bull.* 77, 1914; KEENEY, R. M., "The Manufacture of Ferroalloys in the Electric Furnace," *Trans. A. I. M. E.*, **82** (1920), 28.

trol or the chromium will oxidize out of the metal. Low-carbon ferrochromium may also be made by silicon reduction in the electric furnace and by the thermit process.

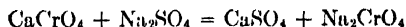
In production of 6 to 8 per cent carbon metal, a recovery of 90 to 95 per cent of the chromium is obtained, because excess carbon is permissible and because fluxing materials, which tend to result in higher carbon metal, can be charged, giving a more fluid slag and resulting in better separation of slag from metal.

On 4 to 6 per cent carbon alloy the recovery of chromium varies from 70 to 80 per cent. About half of this loss is in metallic particles which do not settle out of the slag, practically all of which can be recovered by wet concentration. The power consumption in smelting 44 per cent  $\text{Cr}_2\text{O}_3$  ore in a 750-kw. furnace to produce 4 to 6 per cent carbon alloy averages 3 to 3.5 kw.-hr. per pound of alloy.

**Chromates and Bichromates.**—The processes of manufacture of chromates and bichromates of sodium and potassium are similar.<sup>1</sup> In the production of sodium chromate or bichromate, a chromite ore of 40 per cent or more  $\text{Cr}_2\text{O}_3$  content is roasted with sodium carbonate, whereas potassium carbonate is used to make potassium chromates. If the ore contains sulphur, it is sometimes given a desulphurizing roast, because if there is much sulphur present sodium sulphate forms during the soda roast, and later dissolves with the sodium chromate. The calcine is then mixed with sodium carbonate and limestone and roasted in a reverberatory furnace for 8 to 16 hr., care being taken not to melt the charge. Limestone makes the charge more porous and prevents fusion, but does not enter into the following reaction, beyond combining with a small part of the chromium to form calcium chromate if the roasting temperature has been excessive:



During the roast the charge is rabbled at intervals and is finally raked out onto a cooling floor. The chromates are then dissolved by lixiviation in tanks with boiling water. Calcium is precipitated as calcium sulphate by the addition of sodium sulphate, leaving the chromium in solution according to the reaction:



The solution is decanted and filtered and evaporated to a density of 1.5 to 1.56 sp. gr., 48 to 52°Bé. Conversion of the solution to the bichromate can be accomplished at this point or sodium chromate crystals produced by further evaporation. If a pure bichromate is desired, sodium chromate crystals are produced, washed in a centrifugal, dried and heated, when they crumble to a yellow anhydrous powder containing about 95 per cent sodium chromate. This powder is dissolved in hot water, giving a 40°Bé. solution, 1.38 sp. gr., for conversion to the bichromate.

Addition of sulphuric acid to the chromate solution converts it to the bichromate according to the reaction:



When the solution cools, sodium sulphate crystallizes out, and the bichromate solution is decanted, filtered, and evaporated with the formation of sodium bichromate crystals, which in the crystalline state have the formula  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ . By application of heat the water of crystallization is driven off. Sodium bichromate is replacing potassium bichromate for commercial uses, because of its lower cost and greater solubility.

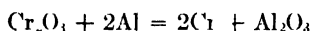
<sup>1</sup> ROSCOE and SCHORLEMMER, "Treatise on Chemistry," vol. 2; BORCHERS, "Metallurgy."

## PROPERTIES OF CHROMATES AND BICHROMATES

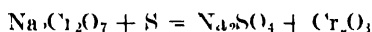
	Potassium		Sodium	
	Bichromate ( $K_2Cr_2O_7$ )	Chromate ( $K_2CrO_4$ )	Bichromate ( $Na_2Cr_2O_7 \cdot 2H_2O$ )	Chromate ( $Na_2CrO_4 \cdot 10H_2O$ )
Specific gravity	2.60	2.71		
Specific heat				
0 to $1^\circ C$	0.1803 + 0.00008 $t$			
19 to $98^\circ C$	0.1894	0.1851		
307 to $484^\circ C$ <sup>a</sup>	0.335			
Latent heat of fusion <sup>f</sup>	29.8			39.2
Melting point <sup>b</sup>	$400^\circ C$	$940^\circ C$		
Solubility				
Cold water	1.10	1.2	7.4 <sup>b</sup>	77.100 <sup>b</sup>
Boiling water	1.1	1.17	Very soluble	Soluble
Alcohol	Insoluble	Insoluble		
Acids	Soluble	Soluble	Soluble	Soluble

<sup>a</sup> Liquid<sup>b</sup> Anhydrous saltSpecific heat  $Cr_2O_3$ , 10 to  $99^\circ C$  = 0.1796Specific heat  $16CrO_4$ , 19 to  $50^\circ C$  = 0.1590

**Chromium Metal.**— Chromium metal is produced commercially by the thermite process, that is, the reduction of chromic oxide by aluminum according to the exothermic reaction



To provide chromic oxide, sodium bichromate is reduced with sulphur in an externally heated non pot



On solidification, the melt is leached and washed with water, the sodium sulphate passing into solution. All traces of sulphur must be washed from the chromic oxide.

The thermite reduction is made in a magnesite-lined furnace without external heat, because the reaction is exothermic, the heat of formation of  $Al_2O_3$  being 392,600 cal., and that of  $Cr_2O_3$ , 243,900 cal. The chromium metal produced by this process contains some aluminum, but is technically free from carbon and from other impurities if a high grade chromic oxide is reduced. By manipulation of the quantity of aluminum charged, a metal containing 99.5 per cent chromium can be made. Fused chromium metal produced by the thermite process has a brilliant white color.

A fairly pure chromium powder can be made by reduction with carbon in a crucible, the process being similar to the production of tungsten powder. Chromic oxide is reduced by solid carbon at a temperature of  $1185^\circ C$ . For laboratory production of pure chromium, magnesium or sodium reduction is an excellent method.

It is also stated that chromium can be reduced from chromic oxide by calcium carbide (Brit. Pat. 152399).

Chromium is a bluish-white metal which holds its bright silvery luster indefinitely. It is harder than glass, electrolytic chromium having a scleroscope hardness<sup>1</sup> of 75. Its specific gravity at  $20^\circ C$  is 6.92. Chromium has a mean specific heat (0 to  $t^\circ$ , up to  $600^\circ C$ ) of 0.1039 to 0.00000008 $t^2$ . Pure chromium melts at 1520 and boils at

<sup>1</sup> SARGENT, G. J., "Electrolytic Chromium," *Trans. Am. Electrochem. Soc.*, **37** (1920), 479.

2200°C. The melting point is lowered considerably if carbon is present, but its hardness is increased. When in the solid state at 1489°C. just below the melting point it absorbs 352 kg.-cal. per kilogram. With latent heat of fusion of 71 kg.-cal., it absorbs 423 kg.-cal. per kilogram liquid at the melting point. The specific heat of liquid chromium is estimated at 0.24.

Chromium to be cast requires considerable superheating, as it is highly viscous for several hundred degrees after it is melted.

Chromium is attacked slowly in cold hydrochloric acid, but rapidly on heating. It dissolves slowly in dilute nitric and sulphuric acids, but is attacked rapidly by concentrated sulphuric acid with the evolution of sulphur dioxide. Hot concentrated nitric acid does not affect it. Electrolytic chromium<sup>1</sup> is very resistant to corrosion by air, oxygen, or chlorine at temperatures up to 300°C. At a temperature of 1200°C. it oxidizes at about the same rate as nickel. An alloy of 20 per cent chromium and 80 per cent nickel has all the non-corrosive qualities of both metals, and an electrical resistance ten times that of nickel.

**Electrolytic Deposition of Chromium.**—Because of the resistance of chromium to corrosion, chromium plating has commercial possibilities. Good deposits of chromium on iron and copper have been obtained from chromic acid ( $\text{H}_2\text{CrO}_4$ ) solutions containing a small percentage of chromic sulphate ( $\text{Cr}_2(\text{SO}_4)_3$ ), with either chromium,<sup>2</sup> lead, or platinum anodes. The theoretical ampere-hour yield of the pure metal from a valence of 3 is 0.6458 g. and from a valence of 6 is 0.3229 g. The theory of the deposition of chromium from chromic acid, chromic sulphate solutions seems to rest on the formation of a film of basic chromic chromate on the cathode with a very weak acid solution in contact with the cathode, followed by partial reduction of chromic ions to chromous ions and the deposition of chromium from both chromous and chromic ions, together with an abundant evolution of hydrogen.

The deposition of chromium is affected by the percentage of chromic acid and chromic sulphate present, the presence of the latter greatly increasing the yield, by the temperature of the solution, and by the cathode current density. The thickness of the chromium deposit depends on the current density, the lower the current density the thicker the deposit. A deposit 0.5 in. thick has been obtained from a plating solution containing 24.5 per cent  $\text{CrO}_3$  and 0.3 per cent  $\text{Cr}_2(\text{SO}_4)_3$  at a temperature of 20°C. with a cathode current density of 10 amp. per square decimeter. A yield of 0.10 g. chromium per ampere-hour may be obtained under these conditions with a voltage of about 3 volts and with an electrode distance of about 1 in. The 0.3 per cent  $\text{Cr}_2(\text{SO}_4)_3$  is a very essential constituent of the plating solution, as without it only traces of chromium are obtained under the conditions stated.

Electrolytically deposited chromium is hard but malleable, while ordinary chromium is usually brittle. Malleable chromium wire can be produced by the process of E. R. Richardson, of the Westinghouse Co., who electroplates a copper wire, draws down, replates, and redraws until the copper center becomes of negligible amount.

A process of chromium plating said to give wearing surfaces harder than any others known metal finish has been developed by Dr. Colin G. Fink, and is known commercially as "erodon." No details are known.

**Chromium Alloys.**—The most important alloys of chromium are the nickel-chromium alloys, which are the most commonly used resistor materials for electrical appliances, electric-oven heaters and industrial electric furnaces, because of their high electrical resistivity, strength, and resistance to oxidation at high temperatures. Because of the latter property, nickel-chromium alloys are having increasing use as furnace parts as containers in the case carburizing of steel, and for points of support in vitreous enameling of iron and steel. Silicon-chromium alloys can be used for these purposes. Experimentation<sup>1</sup> shows that cementation of chromium and iron occurs when low-carbon steel is packed in a mixture of 45 per cent alumina and 55 per cent chromium in an iron tube and then heated to 1300 to 1400°C. in hydrogen, or in a vacuum or in some neutral atmosphere, for lengths of time depending upon the penetration and concentration of chromium desired. The chromized iron has a high resistance to atmospheric corrosion and to weak acid solutions, is comparatively soft, and takes on a high polish. Stellite,<sup>2</sup> an alloy of chromium and cobalt with a considerable percentage of tungsten or molybdenum, has cutting qualities equal to high-speed steel, but cannot be worked, and must be cast in the shape in which it is to be used.

PERCENTAGE COMPOSITION OF CHROMIUM ALLOYS

	Ni	Cr	Fe	Mn	Si	Co	Mo	C
Nichrome	65 1	11 18	22 36	0 70	0 26			
Nichrome	61 8	13 4	21 86	1 76	0 22			
Chromel C	61 68	12 7	21 02	1 16	0 26			
Chromel C	61 45	10 43	21 16	3 74	0 15			
Nichrome III	82 7	14 1	1 95	0 7	0 24			
Nichrome III	82 36	15 9	0 84	0 48	0 16			
Chromel A	79 85	18 22	0 76	0 92	0 08			
Chromel A	77 1	19 7	0 98	1 72	0 29			
Q Alloy	68 0	20 8	15 0	0 013	1 39			0 12
Silchrome	21 33	6 21	64 18	0 75	6 11			0 139
Stellite	....	10 77	3 11	2 04	0 77	59 5	22 5	0 87
Thermalloy	0 12	25 36	72 43	1 95				0 08

Cast nichrome has the following properties. sp. gr., 8.15; weight per cu. in., 0.29 lb.; Brinell hardness, 160 to 170 with 1,000-kg. weight; scleroscope hardness, 27 to 28; melting point, 1510°C.; specific heat at 100°C., 0.111; and temperature coefficient of expansion per degree Centigrade  $1.62 \times 10^{-5}$

<sup>1</sup> KEILEY, F. C., "Chromizing," Trans. Am. Electrochem. Soc., New York Meeting, May, 1923

<sup>2</sup> HIBBARD, H. D., "Manufacture and Uses of Alloy Steels," U. S. Bur. Mines, Bull. 100, 1915

## PROPERTIES OF ROLLED AND DRAWN NICKEL-CHROMIUM ALLOYS

	Specific resistance at 20°C		Temperature coefficient per degree Centigrade between 20 to 100°C	Coefficient of linear expansion per degree Centigrade 20 to 100°C	Approximate melting point, degrees Centigrade	Maximum working temperature, degrees Centigrade	Tensile strength lb per sq in (annealed)	Specific gravity	Weight per cubic inch, pounds
	Microhms per cm cubed	Ohms per circular mil foot							
193 alloy	92 0	550 0	0 0004	$1.71 \times 10^{-5}$	1415	600	52 000	8 15	0 294
Nichrome	109 5	660 0	0 0002	$1.25 \times 10^{-5}$	1350	1000	100 000	8 15	0 294
Nichrome II	109 5	660 0	0 00015	$1.30 \times 10^{-5}$	1370	1050	100 000	8 15	0 294
Nichrome III	89 5	540 0	0 000187	$1.42 \times 10^{-5}$	1490	1100	110 000	8 5	0 306
Nichrome IV	103 0	620 0	0 000179	$1.32 \times 10^{-5}$	1490	1150	120 000	8 5	0 306

<sup>1</sup> Driver-Harris Co., "Alloys for Electrical Resistance," Data Book R-23, 1923, Nichrome Bull. N-21

	Cold	815°C.
Yield point, pounds per square inch	40,000	20,100
Ultimate tensile strength, pounds per square inch	50,000 to 55,000	24,500
Elongation	1 per cent	4 per cent
Reduction in area	2.5 per cent	4.3 per cent

The application of nickel-chromium alloys as resistors in electric heating is based on several laws of electrical engineering of direct current, is for practical purposes an alternating current in a resistor has a power factor of unity. Ohm's law states:

$$E = IR \text{ and } W = EI$$

where  $E$  = e m f in volts,  $I$  = current in amperes,  $R$  = resistance in ohms, and  $W$  = watts; and if  $t$  = time in seconds and  $H$  = heat expressed in B t u.

$$H = I^2 R t \times 0.0009478$$

$$1 \text{ kw-hr} = 3,412 \text{ B t u}$$

To find the resistance  $R_t$  of a wire at any temperature

$$R_t = R (1 + \alpha t),$$

where  $R_t$  is the resistance at temperature  $t$ ,  $R_0$  is the specific resistance,  $\alpha$  is the temperature coefficient, and  $t$  is the difference in temperature between  $R_t$  and  $R_0$ . As temperature coefficients are generally given only from 20 to 100°C, for temperature over 100°C more accurate results can be obtained by use of the following table. Calculation can be shortened by securing resistance tables from the manufacturer of the resistor material being used.

## COMPARATIVE RESISTANCES AT VARIOUS TEMPERATURES FOR NICKEL-CHROMIUM ALLOYS OF A RESISTANCE OF 1 OHM AT 20°C

(Temperature in Degrees Centigrade, Resistance in Ohms)

Material	20°	100°	200°	300°	400°	500°	600°	700°	800°	900°	1000°
Nichrome	1 000	1 0165	1 0417	1 0645	1 0828	1 0928	1 0960	1 1022	1 1122	1 1257	1 1423
Nichrome II	1 0000	1 0111	1 0242	1 0373	1 0508	1 0623	1 0705	1 0794	1 0630	1 0697	1 0781
Nichrome III	1 000	1 0120	1 0265	1 0408	1 0555	1 0633	1 0657	1 0680	1 0760	1 0880	1 1033
Nichrome IV	1 000	1 0078	1 0170	1 0265	1 0360	1 0440	1 0373	1 0310	1 0334	1 0392	1 0482

## CHAPTER XXXVII

### THE METALLURGY OF MANGANESE

BY ERNEST A. HERSAM<sup>1</sup>

**Divisions of Metallurgy of Manganese.**—The metallurgy of manganese becomes important under three separate interests of industry. Of these, the manufacture of manganese steel is perhaps first, being conducted on the largest scale, and requiring much of the manganese ore that is mined and which is smelted to reduce both manganese and iron. The second branch of the metallurgy is the concentration of the native manganese oxides and other minerals of manganese for use in the arts or further metallurgical manufacture, the enriched oxide being commonly useful as a coloring agent in the ceramic industry, as an agent to discharge the color imparted by iron in glass making, as a depolarizing agent in the manufacture of Leclanché and dry batteries, and for a wide variety of other but less important purposes. The third important use for manganese ore is in the preparation of chemical compounds that are of important service in medicine, sanitation, manufacture, and other varied interests. The producer of manganese ore is compelled to follow all these divisions of the metallurgy to secure the proper marketing of his product.

Of the three divisions of the metallurgy, the first leads to the details of iron and steel manufacture, and is to be considered as a phase of the metallurgy of iron. The second, or ore dressing of manganese, which is the mechanical treatment of the ore, is identical with the mechanical enrichment of many ores other than manganese. In this division, crushing, sizing, and concentrating are adapted commonly to manganese oxides, which are of moderately high density, and in some cases of considerable magnetic permeability. Ore dressing is powerless to separate minerals beyond the state of natural purity in which the aggregates occur in nature. When, therefore, manganese minerals are intimately associated with earthy minerals, or with oxides of iron, infiltrated silica, or the carbonates of calcium or magnesium, no physical separation in the solid state is expected to render a satisfactory concentration possible. Since this condition is a common one in the ore of this metal, hand sorting often is found to be the only treatment that is justified. The chemical treatment of the ore to purify the mineral or extract and deposit the manganese in chemical forms that can be employed in manufacture and trade leads to complex chemical relationships. These have to be understood in a broad way to master or to conduct practically the chemical treatment. The metallurgy of manganese, therefore, partly falls under this division.

**The Commercial Production of Metal.**—The commercial production of metallic manganese from the ore practically requires reducing smelting. The reduction of the oxide to metal, it is true, occurs at a roasting temperature without fusion, but the melting to produce metal of form suitable for most use demands costly

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smelting furnaces and presents difficulties exceeding the common ones of smelting. The manganese, upon smelting, is found highly volatile at the required temperature. A loss of 15 per cent from this cause is common experience. The manganese oxide, moreover, inclines to enter the slag.

It becomes necessary, therefore, to smelt the ore at a high temperature, maintaining a strong reducing action throughout the operation, if smelting is carried on in the blast furnace. Such reduction results in the reduction also of all of the iron, which collects in the metallic product. Thus, though a high content of manganese may be desired, an alloy of manganese with iron is obtained. Silicon, also, becomes reduced along with manganese in smelting, the amount depending upon the amount present and upon the character of the slag. Carbon, moreover, is inseparable from the product under the reducing conditions, and is present in the metal to the extent of 5 to 6 per cent. For these reasons it is not possible to smelt lean manganese ores with economy, nor, in fact, owing to the almost universal presence of iron and silica with manganese in ores, is it possible to produce pure manganese by commercial smelting. The best that can be done commercially is to produce a high-grade ferromanganese by the smelting. In smelting iron ore containing manganese to produce pig iron of 3 to 4 per cent manganese, the large amount of slag commonly occasions a heavy loss, carrying 3 per cent or more of manganese. This loss, together with the volatilization, makes it necessary to use ore of not less than some 9 per cent manganese to secure the recovery of this small amount of manganese in the product if desired. The production of a tolerably high-grade manganese product can thus be accomplished only by employing high-grade manganese ore, and making provision in that case for receiving in the metallic product the entire iron content of the ore, which must then be held low. These conditions thus render it necessary to enrich the manganese minerals by hand sorting, or other ore-dressing methods if possible, before smelting. This is often a most unsatisfactory process, owing to the close association of the manganese minerals with barren and harmful minerals, limiting the commercial practice to ore of high grade.

**Mechanical Enrichment.**—An important part of the demand for manganese material is for the oxide or peroxide. From these oxides numerous refined chemical compounds of a varied nature are manufactured. In the supply of the oxides or chemical compounds the manganese may be recovered from the ore by chemical extraction and converted into the required forms by subsequent manufacture. For the purpose of chemical extraction a low-grade ore is sometimes used, but wherever mechanical enrichment directly permits of producing the desired final material, as, for example, manganese dioxide, the ore-dressing methods are greatly preferred. Often the manganese mineral is so closely associated with insoluble silicates as to render it practically impossible to recover it, either by ore dressing or by the processes of chemical extraction. Sometimes it is harmfully associated with alkaline-earth minerals which are soluble in the solvents for manganese. Even thus, when chemical extraction may be contemplated, mechanical enrichment as a preliminary step may be desired.

In many cases, moreover, ore dressing may fail to produce concentrate suited to chemical extraction. Ore dressing therefore, may be preliminary to: (1) smelting to produce ferromanganese, spiegel iron, or low-manganese pig iron; (2) lixiviation to produce manganese oxides or other compounds; and (3) the preparation of various rough coloring ingredients for use in the manufacture of construction materials, or components for fertilizer or other uses. For all of these purposes the principles of gravity concentration and magnetic concentration are applied.



**The Hydrometallurgy of Manganese.**—The wet-treatment of manganese ore requires a knowledge of the manganese minerals and the compounds of manganese that appear in solutions, precipitates, minerals, and products. The chemical and physical agencies that produce effects are the basis of the hydrometallurgy of the metal. These matters are here discussed.

**The Minerals of Manganese.**—The most valued minerals of manganese are the dioxides, of which *pyrolusite* ( $\text{MnO}_2$ ) is the most important. It is a soft bluish-black or grayish-black mineral, 4.8 in density, containing combined water not exceeding generally 2 per cent, and containing, often, hydrous silica in combination or intimate association. *Polianite* is the anhydrous variety of this mineral, 5.0 in density, crystalline, and much harder. *Psilomelane*, corresponding also to the formula  $\text{MnO}_2$ , is a grayish-black mineral, lustrous, massive, and hard, of 3.7 to 4.7 in density. It contains often much combined water, variable in amount, and usually also barium oxide, or potassium oxide, and sometimes the oxides of calcium or magnesium. *Wad* is the soft hydrous variety of the dioxide mineral. *Asbolite* and *lampadite*, and other minerals containing the dioxide of manganese, combined with oxides of other base metals, are known but are uncommon. *Hausmannite* ( $\text{MnO}_2 \cdot 2\text{MnO}$ ), of lower oxygen content than the above minerals, is a firm brownish-black mineral of 5.0 in density. *Manganite* ( $\text{MnO}_2 \cdot \text{MnO} \cdot \text{H}_2\text{O}$ ) is a gray mineral, somewhat softer and of 4.2 to 4.4 in density. *Franklinite* ( $(\text{Fe}, \text{Mn}, \text{Zn})\text{O} \cdot (\text{Fe}, \text{Mn})_2\text{O}_3$ ) is hard, black, and 5.07 to 5.22 in density. *Rhodochrosite* is the carbonate ( $\text{MnCO}_3$ ), pink in color, and 3.45 to 3.60 in density. Combined with iron or calcium carbonate, and sometimes with magnesium or cobalt carbonates, the mineral is given the name *oligonite*. *Rhodonite* ( $\text{MnO} \cdot \text{SiO}_2$ ) is the silicate, the manganese component of which sometimes is partly replaced by iron, calcium, or zinc, and which is reddish in color and 3.4 to 3.68 in density. *Braunite* ( $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$ ), of brownish-black color and submetallic in luster, is 4.7 to 4.8 in density. Other silicates of manganese in combination with the silicates of the base metals are known but are rare. The sulphates and other native salts of manganese occur in nature but do not constitute working ores.

**Manganese Metal and Compounds.**—Manganese is notable for the diversity of its chemical forms. Varying in its state of oxidation from a bivalent element to a heptavalent one, it ranges from a basic-combining element at the one extreme to a highly acid one at the other, entering in its highly oxidized state into numerous acid forms or radicals. In its lower state of oxidation it resembles magnesium and ferrous iron. Somewhat more highly oxidized it resembles aluminum and ferric iron. Still more highly oxidized, it acquires characteristics resembling titanium and sulphur. Finally, in the most highly oxidized forms, it resembles chlorine and other halogens. In its mineral state, and in its metallic comportment, it perhaps most resembles iron. The approximate similarity of its atomic weight, which is 55, with that of iron, which is 55.9, leads often to regarding the element as an equivalent in slags. The high native oxides, however, acquire a stable state which iron does not attain. Many of the compounds of lower oxidation are strikingly similar to those of iron. In many cases these are isomorphous with those of iron, being inseparable by crystallization.

**Metallic Manganese.**—Manganese is a reddish-gray, brilliant metal, harder and somewhat heavier, and more difficult to melt, than iron. It combines as

iron does with carbon, but with greater avidity. It is attacked by acids with much greater energy than iron, and is dissolved rapidly by all ordinary dilute acids inclusive of acetic acid, evolving hydrogen copiously and producing manganous salts. Its affinity for sulphur and for oxygen at high temperatures is utilized in the metallurgy of iron for the deoxidation and desulphurization of that metal. The stability of the simple oxide renders it impossible to reduce and smelt the metal apart from metallic impurities, if present, and the affinity for carbon and metalloids at high temperatures renders it difficult to produce the metal by any means without contamination.

For producing the purest metal, the process of Goldschmidt, consisting of reduction by aluminum, best serves. For this reduction, a purified manganomanganic oxide is used as the source of the manganese, the aluminum powder being incorporated with oxide and raised in temperature to effect the reaction, sufficient aluminum being employed to produce sesquioxide of aluminum from the total oxygen content of the purified manganese oxide. Some 90 per cent of the metal may be so recovered without difficulty in a product of 96 per cent manganese free from carbon. Silicon, iron, and aluminum are the impurities of metal so produced, great difficulty being found in removing the final traces of these metals. The electrolytic deposition of manganese from sulphate solution is possible. The metal is deposited at the cathode from solutions containing free acid not exceeding 0.36 per cent with 80 to 90 per cent current efficiency at 3 volts or more. The deposit is powdery, and no means have been discovered for improving the condition for commercial use.

Numerous processes are in existence for the production of metallic manganese of tolerable purity freed from much of the combined impurity with which the ore is generally associated. By the process of J. T. Jones<sup>1</sup> manganese ore containing iron is finely ground, mixed with coal, and calcined at about 1090°C. with air excluded, to reduce the iron. The iron is removed and the coked product is smelted to produce metallic manganese of grade according with the extent of the preliminary separation of the iron. Sternberg and Deutsch, as early as 1893,<sup>2</sup> produced metallic manganese by igniting the oxide of manganese when combined with alkaline-earth oxide at a temperature ranging from 1000 to 1200°C. in the presence of carbon. Other metals, such as molybdenum, tungsten, and titanium, were also included in the patent. Greene and Wahl, in 1895, prepared manganese, free from iron, by leaching the ore with dilute sulphuric acid to remove iron, leaving the dioxide of manganese unattacked. The purified material was then ignited to produce  $Mn_2O_3$ , followed by the application of volatile hydrocarbons in the treatment and a final reducing treatment with aluminum and magnesium in crucibles.

**Ferrous Alloys.**—Ferromanganese is the common commercial form of metallic manganese. In this alloy some 75 to 80 per cent of manganese is present together with about 6 per cent of carbon, the remainder being mostly iron. Humbert decarbonizes ferromanganese<sup>3</sup> by heating to a temperature above 1700°C. in contact with manganese oxide, in an electric furnace, reducing the carbon content thus to less than 1 per cent. Spiegel iron produced by blast-furnace smelting commonly contains 15 to 20 per cent of manganese and approximately 5 per cent of carbon, the remainder being mostly iron. A lower-grade manganese product with iron is also produced by smelting iron ore when insufficient manganese is present to produce spiegel iron. In the production of metal of this type the tend-

<sup>1</sup> U. S. patents 1288422 and 1289799.

<sup>2</sup> Eng. patent 13177.

<sup>3</sup> U. S. patent 1228025.

ency of the manganese to enter the slag, and the required maintenance of special smelting conditions to effect the recovery of the manganese, introduce costs that commonly detract from the economy of recovering this small proportion of manganese along with the preponderance of iron that also must be reduced. A German patent<sup>1</sup> effects a partial separation of manganese from iron occurring in ores, by reducing the mineral under delicately controlled conditions so as to produce metal from the iron oxide, leaving the manganese oxide unreduced. The reduced material is then smelted under conditions calculated to leave the state of oxidation unchanged, recovering the iron as metal, and the manganese as a rich slag suitable for the production of ferromanganese.

**Non-ferrous Alloys.**—Manganese which appears as an important component of numerous ferroalloys is a less common component of non-ferrous alloys. The manganese-gold alloy is brittle and gray in color, becoming yellow with gold exceeding some 90 per cent and forgeable at this higher percentage of gold. The composition of manganin, a useful alloy, calls for 12 per cent manganese, 4 per cent nickel, and 84 per cent of copper. Manganese to the extent of some 2.8 per cent in brass effects a marked increase in the hardness and tensile strength. The introduction into bronze has been effected by various means as, for example,<sup>2</sup> by alloying the ferromanganese with phosphorus and copper, and introducing this richer alloy into the mixture of the other metals. Manganese is made to alloy in small amount with copper and lead<sup>3</sup> by adding the oxide with cryolite together with a reducing agent to the other metals in the molten state. Manganese when accompanying copper in commercially pure iron increases the effect of the copper, which in proper amount decreases the susceptibility to corrosion and decreases the red-shortness of the metal that is occasioned by the influence of the copper alone.

**Divalent Manganese Compounds.**—Divalent manganese imparts a usual reddish cast to substances containing it. It is to be regarded perhaps as the most stable form in which manganese enters chemical compounds. The divalent manganous salts, for example, are distinguished from ferrous salts by not being susceptible to oxidation in acid solution by the action of the air when present. *Manganous hydroxide* ( $\text{MnH}_2\text{O}_2$ ) is a pink precipitate produced by adding alkali to solutions of manganous salts. It is insoluble in an excess of the alkali, but dissolves in ammonia, changing, when thus alkaline, as it would do when neutral, to the brown manganic hydroxide by exposure to the air. Manganous hydroxide precipitated by ammonia in the presence of cyanuric acid develops unstable colorless crystals of a high polarizing power serving for microchemical recognition. *Manganous oxide* ( $\text{MnO}$ ) is a greenish substance, obtained by calcining the carbonate or by precipitation from heated solutions of manganous salts. It may be obtained by the reduction of the higher oxides, but is with difficulty obtained free from other oxides. *Manganous sulphate* ( $\text{MnSO}_4$ ) crystallizes with 7 molecules of water, and is analogous to ferrous sulphate. It also crystallizes with 5 molecules of water, being then analogous to copper sulphate. It crystallizes, moreover, with 4 molecules in characteristic reddish crystals. It yields monoclinic double salts with alkaline sulphates, of such composition as  $\text{K}_2\text{SO}_4 \cdot \text{MnSO}_4 \cdot 6\text{H}_2\text{O}$ .

<sup>1</sup> Ger patent 303507, Apr 24, 1917.

<sup>2</sup> U S patent 1214330

<sup>3</sup> U S patent 1228017

In 1894 A. R. Davis<sup>1</sup> provided for the extraction of manganese in the form of sulphate from the oxide ore by means of ferrous sulphate, producing commercially manganous sulphate by evaporation. By the process of C. Ellis<sup>2</sup> material containing basic manganese compounds is converted to the sulphate by treatment with acid-sodium sulphate, which subsequently is converted to the dioxide. Numerous methods of production are found possible, further consideration to the matter being given in connection with the methods of producing the dioxide. *Manganous dithionate* ( $\text{MnS}_2\text{O}_6$ ) is formed by the action of sulphurous acid upon manganese dioxide in the cold. It is soluble in water and convertible into sulphate by oxidation. *Manganous carbonate* ( $\text{MnCO}_3$ ) is a reddish precipitate when formed by the addition of alkaline carbonates to manganous salts. It is less susceptible to oxidation than the hydrate. *Manganous sulphide* ( $\text{MnS}$ ) forms as a flesh-colored gelatinous precipitate from alkaline solutions by the action of alkaline sulphides. Precipitation from moderately strong, hot solutions sometimes gives the precipitate the form of a greenish-gray powder. The sulphide is very readily attacked by the oxygen of the atmosphere or by any ordinary weak acid, yielding hydrogen sulphide and the manganous salt of the acid. *Manganese borate* is precipitated from manganous solutions by borax. As commonly prepared, it is in the form of a brownish powder. It possesses valued catalytic properties, notable use for which is in the acceleration of the drying of vegetable oils, which is a process of oxidation. It thus becomes an important component of commercial driers required in the paint and varnish industry, in which application it acts catalytically. *Manganese resinate* and *manganese linolate* are also similarly serviceable in this use. In preparing the resinate, a rosin soap is first made by boiling rosin in caustic soda, which is then poured into manganous sulphate solution, producing a flesh-colored precipitate, which is the resinate, and which is filtered, washed, and dried, being then soluble in hot linseed oil or in any one of a variety of organic solvents, such as chloroform. It is capable of being melted, and when cooled forms a brown mass that may be broken into lumps of similar solubility and suitable for handling. Four pounds of this material in 10 gal. of linseed oil give quick drying oil, leaving a glossy coat, or, when less is used, a pale drying oil. The linolate is produced by boiling linseed oil with caustic alkali. This soap is then added to manganous sulphate or chloride, producing a brown mass which is subject to oxidation and which is readily soluble in hot linseed oil. One part of this linolate mixed with five of linseed oil and poured hot into 10 gal. of oil at  $250^\circ\text{C}$ . produces a desirable drying oil.

**Manganic Compounds.**—The manganic compounds are much less basic in action than the manganous. In acid solution, the salt tends to become reduced to the manganous state, while in acid solution salts remaining unreduced are subject to marked hydrolysis, which results in the separation of *manganic hydroxide* ( $\text{MnH}_3\text{O}_3$ ) from solutions of the neutral salts. The manganic hydroxide may be made readily to part with its combined water, forming a partly dehydrated hydroxide, manganite ( $\text{MnOH}$ ), or the anhydride ( $\text{Mn}_2\text{O}_3$ ), both of which occur in nature as minerals, whereas the hydroxide does not.

The preparation of pure *manganic sulphate* ( $\text{Mn}_2(\text{SO}_4)_3$ ) or the *chloride* ( $\text{MnCl}_3$ ) is rendered difficult by the tendency of the salt to hydrolyze, making it necessary, in preparing the sulphate, for example, from the oxide, to employ strong acid in the reaction, and rendering it difficult to remove the foreign salts from the paste of sulphate except by means of nitric acid. Manganic chloride also forms in strong solution, but is unstable when deprived of the excess of strong acid. The *fluoride* and the *phosphate* of manganese, in this state of oxidation, are red and violet in color and

<sup>1</sup> Eng. patent 2896.

<sup>2</sup> U. S. patent 1276739.

hydrolyze much less readily than do the other salts. These salts form double compounds with the alkalis, producing striking crystalline aggregates.

**Tetravalent Manganese in Compounds.**—The perhydroxide of manganese ( $\text{MnH}_4\text{O}_4$ ) is produced by the action of strong oxidizing agents upon the alkaline or neutral hydroxide. For the purpose, chlorine, bromine, or hypochlorite may be used. It is a dark-brown substance, amorphous, and easily converted into a colloidal state. In this state of oxidation manganese formerly was employed extensively in the production of chlorine.

Thus when the perhydroxide is treated with strong cold hydrochloric acid, it dissolves, giving a dark-green manganic *perchloride* ( $\text{MnCl}_4$ ). This salt hydrolyzes when diluted, producing again the perhydroxide, or decomposing into chlorine and manganous chloride upon warming. The perhydroxide, subjected to moderate dehydration without the presence of reducing agents, produces the partly dehydrated perhydroxide ( $\text{MnO}(\text{OH})_2$ ) which becomes peroxide upon further dehydration. In producing chlorine from these compounds, a dioxide of manganese is treated with hydrochloric acid to produce the tetrachloride, which, upon elevated temperature, liberates  $\text{Cl}_2$  and becomes manganous chloride ( $\text{MnCl}_2$ ). The famous Weldon process consists in rendering this manganous chloride alkaline, with an excess of lime, which in the presence of the excess of lime becomes oxidized to calcium manganate ( $\text{CaMnO}_3$ ), known as "Weldon mud," containing the manganese again in the tetravalent state suitable for further acidification with hydrochloric acid and the further generation of chlorine.

The *peroxide of manganese*, or *dioxide* ( $\text{MnO}_2$ ), is unstable at elevated temperature, and yields its oxygen to compounds capable of receiving it at that temperature. Thus, in the manufacture of glass, the peroxide discharges the green color of ferrous silicates by producing the less highly colored ferric silicate. Its presence assures a high state of oxidation of iron in ceramic material, imparting a brown or a violet color by the direct coloring action of the manganese oxide itself in silicate or other combinations. As a decolorizer for glass, manganese material of 80 to 85 per cent dioxide is commonly wanted, containing less than 1 per cent iron. Such material is used in glass to the extent of some 4 to 30 lb. to the ton of sand, in many processes of manufacture. While a siliceous ore is permissible for application to this purpose, the presence of carbonates is objectionable. For making glass in pots, powdered ore is used, while the ore in lump form may be used in some cases for melting larger masses. The dioxide is used direct as a drier for linseed and other drying oils in amount generally not exceeding 0.5 per cent. In this form it meets with the objection that it darkens the oil, to a greater extent than the sulphate, borate, oxalate, resinate, or linoleate. As a dyeing material for cotton the chloride is used, in many cases, as it imparts a brown color to the cotton fiber. Much manganese dioxide is consumed in the manufacture of manganates, chiefly in the production of the permanganates. The dioxide is reported to be converted into a colloidal form by adding concentrated ammonia to  $N/20$  potassium permanganate solution until the color becomes deep brown, resulting in a solution that remains stable in the presence of alcohol of any density.

**Manganese Dioxide as a Depolarizer.**—The peroxide of manganese as a depolarizer for the manufacture of galvanic cells is of great importance. The physical form of the peroxide influences the effectiveness in a marked way, and the presence of soluble metallic impurity is of great injury. The largest consumption of manganese dioxide, outside that of iron manufacture, is to make use of this action in the manufacture of dry cells and other galvanic-battery elements. In

this use the available oxygen, in excess of that required to constitute manganous oxide, governs the effectiveness and value. Freedom from metals that are electronegative to zinc, such as copper, nickel, cobalt, and arsenic, is especially important, copper being most objectionable. Such metals cause local corrosion upon the zinc of the cell.

Caucasian pyrolusite of some 85 per cent manganese dioxide containing less than 1 per cent iron is commonly desired, yet ore of 70 to 80 per cent dioxide and 3 to 4 per cent iron is often used when suitable in other respects. Moderate hardness and a certain slight degree of porosity of the mineral are desired, even at the sacrifice of the highest oxygen content. Sized, crushed material is employed which is commonly finer than 10 to 20 mesh. In the Leclanché cell, a depolarizing mixture of manganese dioxide with graphite is often used. The artificial dioxide free from acid and containing occluded moisture may be used with a low proportion of graphite.

A hydrated dioxide of manganese for depolarizing purposes has been prepared<sup>1</sup> by the oxidation of dilute acid solutions of sulphates or chlorides, or by the treatment of the oxide with water, glycerol, and acid. In the process of A. A. Wells,<sup>2</sup> dioxide for battery purposes is prepared by converting the oxide ore into carbide, treating in water to produce manganous hydroxide, and roasting in an oxidizing atmosphere containing steam. By the subsequent process of Ellis and Wells,<sup>3</sup> dioxide, suited to the purpose, is made by permitting a hypochlorite to act upon a slightly acid solution of manganous salt at about 100°C. A dioxide which gives a dead-black streak and is suitable as a depolarizer is produced under the patent of Ellis,<sup>4</sup> by exposing manganous sulphate solution, containing not more than 10 per cent free acid, at a temperature near the boiling, to the action of chlorine. The precipitate is recovered and washed free from contaminating salts. The depolarizing material of batteries has been regenerated, for example,<sup>5</sup> by crushing the material, extracting the soluble salts by means of ammonium chloride solution, and reoxidizing the residue by treatment under pressure with hypochlorous acid or its salts, or by chloric acid.

In electrolysis, manganese salts incline to throw out the dioxide at the anode. This deposition ensues in result of the hydrolyzation of the tetravalent manganese ion with a relatively complete breaking down of the hydroxide to the dioxide at the anode surface. The nature and the state of the cathode material influence the required e m f in practical operation, which will be higher than 1.35 volts, the potential gradient between the dioxide and the manganous ion. In sulphate solutions, at the ordinary temperature of the air, deposition of the dioxide commonly occurs under an e m f of approximately 2, the current efficiency decreasing with increasing acidity. At 70 to 75°C practically 100 per cent current efficiency is secured. The decline of efficiency with increasing acidity does not prevail at this temperature as in the cold, thus permitting of the employment of 20 per cent acidity in extreme requirements.

**Production of Manganese Dioxide from Ores.** The manufacture of manganese dioxide from ores consists in the extraction of the metal as a salt, held in solution at a low state of oxidation, and its release as dioxide by the agency of an oxidizing process. There are numerous processes of this type capable of operation with high efficiency and chemical completeness. These, however, are brought into competition with production from a varied supply of the native peroxide of tolerable purity that is often adequate. Some of these processes have been long

<sup>1</sup> U. S. patents 1269913, 1269914, 1269915 and 1269916

<sup>2</sup> U. S. patent 1293272

<sup>3</sup> U. S. patent 1330738

<sup>4</sup> U. S. patent 1289707.

<sup>5</sup> Ger. patent 315335.

known, and have continued to render economic service for many years. Others have been stimulated by relatively modern interests and possibilities. An order of chronological sequence is observed here in the presentation.

An early and important use, which has continued to be made, of the production of manganese peroxide is in the regeneration of the calcium manganate, which may be regarded as a combination of the peroxide of manganese with calcium oxide. This appears in a step of the Weldon process, which at an early time was the only practicable process of cheaply manufacturing chlorine. The process has already been described (p. 1270). The Herrenschmidt and Constable process consisted in applying ferrous sulphate at the ordinary air temperatures to manganese ore for the extraction of the metal in the form of manganous sulphate, recovering also cobalt in a similar form, if present, and leaving the iron in the state of ferric oxide as a residuum in the vat, thus obtaining a manganese solution for such precipitation as is desired. In 1884 Readman secured an English patent for impregnating ore with a solution of ferrous chloride, heating in a suitable furnace to decompose the chloride, and forming the chlorides of manganese as well as nickel and cobalt, if present, relatively free from iron for the precipitation of dioxide.

The German patent of Nithack, issued in 1884, provided for spraying the dissolved chlorides extracted from ore upon hot inclined plates of fireclay in the presence of atmospheric oxygen, causing the release of hydrochloric acid and the production of an oxide of manganese of a lower state of oxidation than the dioxide. In 1884 an English patent was granted Herrenschmidt to use ferrous chloride solution as a solvent to extract manganese and nickel and cobalt, if present, from the finely pulverized ore, followed by the precipitation of the nickel and cobalt upon manganese sulphide, or hydrated manganese oxide, and recovery of the manganese sulphate by evaporation, or the oxide and hydrochloric acid by calcination. Further improvements of the Herrenschmidt and Constable process, in 1885, consisted in boiling the fine manganese or cobalt ore with ferrous sulphate, followed by decantation and oxidation of the sulphate.

The Dunlop process consisted in calcining the native or artificial carbonate of manganese to produce oxide of manganese, attempting a high state of oxidation by the calcining or roasting action, elevating the temperature to 300 to 400°C., and maintaining oxidation for 36 hr in a special furnace in which the material was supported in small wagons with provision for the propulsion of these. M. A. Reyehler shortened the duration of the roasting of the Dunlop process to approximately 1 hr., showing that 80 per cent dioxide could be obtained under the conditions. More effectively to destroy residual carbonate, Reyehler moistened the manganese oxide ore with dilute nitric acid, allowing it to dry before calcining, whereby, at 125 to 260°C., nitrous fumes escape, accounting for some 10 per cent of the total nitric acid, and manganese dioxide of at least 91½ per cent purity is obtained.

By the Kuhlman process, nitric acid is applied in the calcining of the native oxide or carbonate, sufficient acid being used to convert all manganese to the form of nitrate before calcination. Campbell and Boyd in 1893 produced manganous carbonate, suitable for the Dunlop process, from waste sulphate liquors by precipitating with sodium carbonate solution, following by washing and drying. In the same year Albright and Hood used coal dust in conjunction with sulphuric acid in calcining manganese oxide to produce manganous sulphate to be recovered by subsequent aqueous digestion. The sulphate was converted to chloride by calcium chloride and the precipitated calcium sulphate separated. The chloride was then concentrated and the manganese converted to the tetravalent form of calcium manganate by the addition of lime and the characteristic oxidation of the Weldon process. Albright and Hood further developed the precipitation of manganese in the form of hydroxide from

the sulphate solution by ammonia, recovering the excess ammonia upon evaporation and oxidation of the precipitated hydrate.

Chapman's patent for producing manganese dioxide consists in roasting manganese carbonate with a chloride salt. By the process of C. J. Reed<sup>1</sup> aqueous manganese sulphate is heated with nitrate salts, leaving manganese dioxide in the residue. By the process of Dutt & Dutt, the oxide ore and alkaline hydroxide are roasted at 600 to 750°C. in a current of air in a reverberatory furnace, producing manganate, followed by lixiviating the roasted mass to remove iron as ferric hydroxide resulting from the reaction upon ferrites if present. The manganate solution is then decanted, evaporated, and heated in a retort to 500°C. in an atmosphere of steam, producing a resulting mixture of manganese dioxide and alkaline hydroxide, which is washed to remove alkali, and dried.

The Vadner process consists in bringing sulphurous gas from roasting sulphide ores, or produced by the burning of sulphur, into contact with manganese oxide ore of 5 to 35 per cent. This has been done by spraying the fine pulp into the gas. Silver and base metal, such as zinc, are attacked and dissolved along with the manganese. Iron is precipitated by finely divided calcium carbonate, and the zinc is separated and recovered by precipitation with the like precipitant at a higher temperature. Finally, lime and air are used to precipitate the dioxide. A later improvement of the process consists in leading the pregnant manganese solution over manganese dioxide to precipitate lead and iron, and treating with chlorine to produce the dioxide of manganese. Zinc and lead are both recovered. The manganese product never falls below 90 per cent manganese dioxide, and under average conditions exceeds 99.5 per cent.

The process of Haslup and Peacock<sup>2</sup> consists in digesting for 15 hr. or more the finely ground, low-grade ore with added salts, such as ferrous sulphate, aluminum sulphate, or salts of potassium, that will contribute to the heat of reaction along with sulphuric acid not exceeding 55°Bé. The treatment is conducted in a heat-insulated container at a temperature of 150°C. By further patent,<sup>3</sup> the action of the free sulphuric acid is relied upon as the source of heat. In any case the temperature is developed and maintained by the reaction. The digestion is followed by the extraction of the sulphate in water in a condition suitable for conversion to the dioxide.

By the process of M. L. Kaplan<sup>4</sup> manganese carbonate is converted to the oxide by exposure to air containing nitric oxide at some 300°C. The decomposition product is recovered by heating the sulphuric acid solution containing it and which is passing from the oxidation chamber. The chief reaction of the oxidation is as follows:



The lower oxide of nitrogen is converted to the higher state by the action of air. By Kaplan's subsequent patents<sup>5</sup> provision is made for the treatment of native carbonate ore, or ore containing basic mineral, by the action of nitric acid, removing the excess of nitric oxide by the application of heat and producing dioxide suitable for battery purposes.

**Sulphurous Acid Process of Van Arsdale.**—By this process<sup>6</sup> the manganese oxide ore, of 18 to 20 per cent manganese, reduced by crushing to 30 mesh, and containing water sufficient to produce a mobile pulp, is exposed to the action of sulphur dioxide as contained in roaster gas. The appliance that has been used for the absorption of the gas is the revolving cylinder of the Leaver type, with

<sup>1</sup> U. S. patent 1415305

<sup>2</sup> U. S. patent 1279108 and 1279110

<sup>3</sup> U. S. patent 1291867

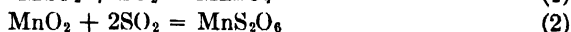
<sup>4</sup> U. S. patent 1247278

<sup>5</sup> U. S. patent 1293461, 1294462, and 1293463.

<sup>6</sup> U. S. patent 1304222



perforated discs and deflectors. Reaction occurs between the aqueous solution of the gas and the manganese oxide in accordance with one or both of the following reactions:



The treatment is required to be conducted at an elevated temperature, as with gases hot from the roasters. Reaction without this heating results in the less desired effect indicated by reaction (2) above, which in any case cannot be entirely prevented. The dithionate of manganese produced by this reaction thus accompanies the sulphate produced by reaction (1). The treatment consists in a continuous and progressive digestion of the ore, or, when preferable, an intermittent digestion of identical action.

To obtain a manganese solution of high density, as, for example, 1.5 sp. gr., a progressive treatment of at least two steps is necessary, by which the depleted ore receives the action of the fresh gases entering, and the fresh ore imparts higher content to the effluent solution passing from treatment. Solution of density as low as 1.2 sp. gr. may be produced by either the direct or the intermittent procedure. Filtration of the solution resulting from the extraction of the ore is practically necessary, Oliver filters having been used with fair success on solutions of 1.2 sp. gr., or less. No practical way has been found to filter the stronger solution. The clear solution from the treatment, following filtration, is evaporated to dryness in subheated, cast-iron pans, expelling water and sulphurous anhydride from the dithionate and yielding a residuum of manganese sulphate. The firm adhesion of the salt to the pans requires mechanical removal, a chisel in an air hammer at times being required to detach the crusts. The dislodged and digested residue of manganese sulphate is calcined in a rotary kiln, lined with magnesite brick, elevating the temperature at the heated end to 1950°F or higher, and yielding manganese oxide ( $\text{Mn}_2\text{O}_3$ ) in the form of nodules containing less than 0.5 per cent sulphur and of a high degree of purity. Manganese dioxide may be recovered from the heated solution also by electrolysis.

**Sulphurous Acid Process of Westling.**—The American Manganese Products Co., of Redwood City, Cal., is equipped for the manufacture, by E. H. Westling's patented process, of manganese dioxide of a high degree of purity suited to the manufacture of chemical products, glass, and pigments. The product is not, at present, finding the use that should be expected in the dry-battery industry, owing to competition with natural oxide of adequate purity for many uses and of a commonly known and desired physical state. The fine ore, containing dioxide and other oxides of manganese, is crushed to the 20-mesh size or finer, and thence elevated to storage tanks for an intermittent supply at a rapid rate of discharge. The thickened mobile material drawn from the storage tanks enters digesting vats of cylindrical form, provided with conical bottoms lined with acidproof brick bound with the acidproof cement of the Chemical Construction Co.

The digesting vats are provided with corrosion parts and with inner cylinders of a form resembling those of the Pachuca tank. Sulphur dioxide, with a slight excess of air, produced by the combustion of sulphur under pressure in a Schutte & Koerting burner, is conveyed, while warm, to the vat, and allowed to react upon the charge producing manganese sulphate. After digestion with the sulphurous acid solution and with air as described, the manganese sulphate solution and residues are conveyed to a tank where a little powdered calcium carbonate is added, to neutralize the solution

and to precipitate iron and alumina, arsenic, and other impurities. This is done at about 50°C. under constant agitation. Following this treatment, calcium nitrate solution is added while agitation continues, resulting in the production of manganese nitrate, which remains in solution, and of calcium sulphate as a precipitate. The mass, consisting of manganese nitrate solution and residual insoluble material, containing the insoluble residue of the ore, ferric hydroxide, basic iron salts, and other mineral matter, contains also calcium sulphate crystals which coat the particles of the fine slime and render it easy of filtration. This residue is removed by filtration without difficulty by the ordinary Oliver filter.

Copper, when present in the ore and taken into solution by the action of the acid, is precipitated completely by aluminum dust, a separate precipitation treatment for which, when required, is provided. The clear solution of manganese nitrate, freed from copper and to a large extent from its original calcium salts, is evaporated in open pans, where all further and final separation of calcium sulphate occurs, producing crusts easy of removal. The evaporation is continued under pressure in vertical cylindrical retorts with conical bottoms provided with acidproof lining and corrosion parts. By this final evaporation treatment manganese nitrate decomposes, producing pure manganese dioxide, and releasing nitric anhydride, which is recovered by means of scrubbing towers, in series, the first of which produces pure nitric acid of 1.38 sp. gr., used for the manufacture of lead nitrate. The more highly diluted acid recovered from the succeeding towers is brought to the required strength by systematic and progressive absorption of the nitric gases. The pure product is obtained in the form of an easily settled, fine, granular material that is readily washed, settled, dried, and recovered.

**Manganese Oxide as an Interfering Mineral.**—The extraction of silver, and in some cases of other metals, from ores in which the metal of high value is found in close association with the dioxide or other oxides of manganese has been notable for the difficulties that have been encountered. Attempts of many kinds have been made to separate the manganese or to render its influence otherwise negligible. Smelting the ore meets with no interference beyond that common to iron oxides, since manganese in moderate proportion enters slags in the form of oxide, or silicate, as iron would do. When metals are to be extracted by cyanide solvent, however, the interference is marked.

By the process of A. G. French, patented in 1913, manganiferous sulphide ores of zinc, lead, or silver are treated to recover the manganese by roasting at 700°C., followed by incorporating with the ore some 5 per cent of sodium bisulphate, and wet grinding, followed further by leaching, in which treatment sulphates of sodium, zinc, and manganese are extracted. The solution is subjected to electrolysis between anodes of lead and cathodes of zinc, at 2.5 to 4.5 volts and 200 to 300 amp. per square meter of cathodic surface. The manganese content of the electrolyte is controlled to suit the conditions of deposition of the zinc, adding, when necessary, manganese sulphate produced by the action of aqueous sulphur dioxide of the furnace gases upon the manganese dioxide ore, using the spent electrolyte as an aqueous carrier of the sulphur dioxide from the roaster gases and as a solvent of the manganese yielded by the ore.

The Vermaes process<sup>1</sup> for the treatment of manganese-silver ores consists of a reduction roast in the presence of a chloridizing agent at a temperature below the volatilization temperature of silver chloride, followed by extraction with water and the recovery of the silver from the ore by cyanide. Carpenter's process for the treatment of manganiferous silver ores consists in a chloridizing-volatilizing roast at 1000°C.,

<sup>1</sup> U. S. patent 1234426

recovering silver from the collected fume and by the cyanide treatment of the residue. L. W. Austin has patented a process<sup>1</sup> which consists in adding raw pyrite with sulphuric acid to manganiferous silver ores, following by water washing and cyanidation. Many similar but minor expedients of varied sorts have been resorted to in the effort to obtain a satisfactory recovery of the precious metal from ore of this character.

**Physical Properties of Manganese Dioxide.**—The physical properties of manganese dioxide are well observed in the properties of the pure minerals which have been mentioned. It is, however, most difficult to obtain from any source a manganese mineral that may be said to be a dioxide of absolute purity. As a chemical precipitate, produced, for example, by the Westling process, the substance is a grayish-black powder, composed of hard and compact grains. The desired quality for depolarizing purposes and the existence of a colloidal form are elsewhere explained. The dioxide by recent experiment is found to be slowly acted upon by hydrogen or hydrogen sulphide at ordinary temperature and atmospheric pressure, resulting, in the one case, in the formation of a lower oxide of manganese and in the other of the sulphide of manganese. By the process of Clevenger and Caron, manganese-oxide ores are treated to reduce the oxide to a lower state to facilitate recovering manganese by magnetic concentration.

**Compounds of Hexavalent Manganese.**—The hexahydroxide of manganese is not known, nor is the free acid corresponding to its partial anhydride ( $\text{H}_2\text{MnO}_4$ ), which would correspond to manganic acid. The salts of this acid are known, however, and for the alkaline elements are stable and important under certain conditions. These salts are stable also in a state of alkaline fusion. In alkaline solutions they resemble the sulphates in comportment and with them they are in some cases isomorphous. When manganic salts are rendered neutral or acid, depriving the solution of negative ions to support the lower radical, the manganese passes into the heptavalent form and produces the well-known permanganate, a typical salt of which is permanganate of potassium ( $\text{KMnO}_4$ ). In this transition from the hexavalent to the heptavalent form, an oxidizing action is implied, and a draft upon the action of some oxidizing agency is naturally made. When no agent is supplied, the manganic ion ( $\text{MnO}_4$ ) is itself in part reduced, producing the dioxide ( $\text{MnO}_2$ ) and yielding the oxygen required to produce permanganate. Nitric acid facilitates this reaction but does not amply yield the oxygen required. Chlorine and bromine are agents naturally suited to the reaction.

The prevailing color of the manganates is green, while that of the permanganate is violet. The transition from the violet to the green color implies always a change in the state of oxidation when it appears to follow the alteration of the acidity. The green or hexavalent form is highly stable at high temperatures and tends to take oxygen from any available source, as is the case when the dioxide is fused with alkaline hydrates. By its pronounced color it is a common evidence of the existence of manganese in fused mixtures. The alkalinity required for the existence of the manganate state in contact with water renders the salts important chiefly as transition products in the production or employment of permanganates.

**Compounds of Heptavalent Manganese.**—The ready transition of manganates into salts containing the heptavalent anhydride ( $\text{Mn}_2\text{O}_7$ ), resulting in the formation of permanganate, is indicative of the stability of permanganate salts under normal conditions, and under conditions of acidity. In this form the manganese

<sup>1</sup> U. S. patent 1327974.

resembles the chlorine atom which appears in corresponding combinations as perchlorate. Permanganic acid, itself, is stable in acid solution. It can be produced by decomposing barium permanganate with sulphuric acid, which removes the barium as an insoluble sulphate. The attempt to isolate absolutely permanganic acid results in producing the anhydride ( $Mn_2O_7$ ), which is a violet-brown oily liquid, liable to explosive decomposition into oxygen and manganese dioxide. The reduction of permanganate, when employing it as an oxidizing agent, is thus different in result according to the relative presence of acid or base. In acid solutions, permanganates leave the dioxide as a decomposition product. In alkaline solution, the product is a manganous salt. Most substances, whether of mineral or of organic nature, that are conceived as being susceptible to oxidation are attacked and oxidized by permanganate in solutions or added to fusion mixtures.

The alkaline manganates and permanganates are produced in various ways, the principle of the treatment commonly being that of the oxidizing-alkaline fusion of manganese oxides. The action is commonly conducted in kilns by allowing air to react upon finely ground manganese dioxide and alkali. For ample yield and best results it is preferable to employ potassium hydroxide in an amount equivalent to 2.5 molecules for each molecule of the dioxide, maintaining a temperature of some  $300^{\circ}C$ ., and supplying moisture with the air. By the process of Shøeld,<sup>1</sup> the permanganate is produced from the manganate solution, of 1.15 to 1.2 density, by oxidizing electrolysis, using porous anode compartments. The Brewster process<sup>2</sup> provides for the oxidation to permanganate by the application of chlorine to the hot solution. The patents of Lovelace, Lanning, and Judefind<sup>3</sup> are for the production of sodium permanganate from sodium hydroxide by employing anodes of manganese containing tungsten, molybdenum, or silicon in anode compartments. James C. Adell<sup>4</sup> makes use of the presence of the oxide of iron in an oxygenation treatment of alkali and manganese oxide in the presence of air. MacMillan<sup>5</sup> accomplishes the reaction with the alkali by fine comminution of the mixture while at a temperature of  $400$  to  $550^{\circ}C$ . A patent of McCormack<sup>6</sup> provides for mixing manganese dioxide with an aqueous solution of alkaline hydroxide, and evaporating the mixture to dryness, followed by a moderate elevation of the temperature to produce alkaline manganate. By the patented process of Vanderkleed,<sup>7</sup> sodium manganate is produced by the fusion of manganese dioxide with sodium peroxide.

**Analysis of Manganese.**—The chemical determination of manganese with assurance of accuracy in ores, or as a component of iron and steel, has been always an involved and exacting operation. Many methods are known, some of which have been shortened to become methods of convenient assay. The element, when present in iron and steel, commonly requires the longer procedure of quantitative analysis for accurate determination. One may read A. A. Blair on the "Chemical Analysis of Iron," or Sutton's "Volumetric Analysis." The zinc oxide method of Lowe<sup>8</sup> is commonly accepted as being well suited to ores. The method of Clennell<sup>9</sup> is suited to the determination of the manganese alloy with aluminum.

<sup>1</sup> U. S. patent 1281085.

<sup>2</sup> U. S. patent 1291751.

<sup>3</sup> U. S. patents 1291680, 1291681 and 1291682.

<sup>4</sup> U. S. patent 1318432.

<sup>5</sup> U. S. patent 1318891.

<sup>6</sup> U. S. patent 1337239.

<sup>7</sup> U. S. patent 1339242.

<sup>8</sup> Cf. Low's "Technical Methods of Ore Analysis,"

<sup>9</sup> *Eng. Min. J.*, 1918, 407-410.

Manganese accompanying other metals is commonly freed by utilizing the permanence of its salts in acid solution in the presence of hydrogen sulphide, and the stability and insolubility of its sulphide in alkaline solution, iron being previously removed and thus not here under consideration. The manganese, therefore, accompanies zinc, nickel, and cobalt, from which, along with zinc, it is separated by the greater readiness of its sulphide to react with dilute acid. It is separated from ferric iron by the relative solubility of the manganous hydrate in ammonium chloride, and from zinc by the relative insolubility of the manganous hydroxide in alkali. The possible electrolytic deposition of the dioxide upon the anode of the electrolytic cell permits of separation from most other metals, lead being excepted, and, under certain conditions, silver.

**Economic Demands.**—The great demand for manganese arises in its metallurgical use as metal in ferroalloys and the industrial uses of dioxide and the several well-known compounds required in many varied applications. The production of the pure dioxide is seen to be a starting point for the manufacture of most compounds as well as for the preparation of the metal. Manganese minerals and products of low grade have been used for a wide variety of purposes, in some cases as coloring agents, as in the manufacture of terra cotta of required shade, or for cements and other construction materials. The use of manganese as a fertilizer has been shown by years of experience to have been helpful as a crop stimulant in the cultivation of oats, in which case the carbonate is commonly preferred, but is of neutral effect and of little value for most other agricultural uses. Under present conditions, a low content of manganese in ores or minerals signifies little value except where a high degree of concentration or a simple process of chemical extraction becomes possible.

## CHAPTER XXXVIII

### COBALT

BY GORDON C. Mutch<sup>1</sup>

**Cobalt Ores.**—There are few deposits of cobalt ores that are at present being worked. The most important deposits are at Cobalt, Ont.; Missouri; New Caledonia; Belgian Congo; Schneeberg, Germany; and Mount Selwyn, Australia. Some cobalt concentrates are at present being shipped from Mount Selwyn, but the bulk of the cobalt ores now being smelted come from Cobalt. Cobalt occurs, as a rule, associated with nickel. The Missouri deposits are composed of sulphides, the New Caledonia deposits are oxides, and the Cobalt, Ont., minerals are mostly arsenides and sulphides.

In a considerable number of the cobalt minerals cobalt occurs as arsenide, antimonide, sulphide, and oxide associated with iron, copper, silver, and nickel minerals of a somewhat similar nature. Among these may be mentioned: cobalt bloom (erytherite— $\text{Co}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$ ); cobaltite, ( $\text{CoAsS}$ ); smaltite ( $\text{CoAs}_2$ ); niccolite ( $\text{NiAs}$ ); chloanthite ( $\text{NiAs}_2$ ); mispickel ( $\text{FeAsS}$ ).

The geology of the Cobalt, Ont., deposits has been studied exhaustively by Ontario government geologists, and the results of their work have been made the subject of several of the reports of the Ontario Bureau of Mines.

**Metallurgy.**—Technical literature contains little information upon the metallurgy of cobalt as it is practiced today. The cobalt smelters have kept their processes secret, and information about the various methods of smelting is consequently rather scarce. As a result, the industry has suffered somewhat by being deprived of the benefits of the interchanging of ideas and the mutually helpful discussions that are the custom among copper metallurgists. Considerable ingenuity has, however, been exercised by the cobalt smelters on this continent, so that now they are able to compete favorably with the European producers whose processes are considerably older.

In connection with the development of the cobalt industry on this continent, the following description of the first successful smelting operations (1908) on a commercial scale on Canadian cobalt ores is of interest.

The ore was smelted to bullion, speiss, slag, and arsenical fume, very much as has been done since, except that the first smelting furnace was a coal-fired reverberatory. This furnace made speiss very low in iron, say 5 to 7 per cent, and slags that seldom ran less than 30 oz. of silver per ton. The speiss carried 3,500 to 5,500 oz. of silver per ton. The reverberatory furnace was not long used, but was replaced with a small circular water-jacketed furnace.

The speiss was ground in a Krupp mill and roasted in a small hand-rabbed furnace, which it was seldom possible to get hot enough. It was aimed to get rid of all arsenides, but not to make a product very low in arsenic, as the difficulty in doing so

<sup>1</sup> Metallurgical & Chemical Corporation, Mattawan, N. J.

was thoroughly appreciated. It was seldom that the total arsenic in the product was as low as 18 per cent, and 22 per cent was probably the average.

The roasted speiss was screened through a 20-mesh screen, the oversize returned to the Krupp mill and the fines mixed with water and sulphuric acid in a coal-fired mixing pot having a duplex stirring arrangement. Here the metals were practically completely sulphated and a considerable amount of arsenic driven off. When all action had ceased and the material was reduced to a granular condition, sufficient soft coal was worked in to reduce all  $\text{As}_2\text{O}_5$  to  $\text{As}_2\text{O}_3$  and all  $\text{Ag}_2\text{SO}_4$  to metallic silver. By cautiously heating the resulting mixture with exclusion of air, the  $\text{As}_2\text{O}_3$  could be mostly driven off; the residue containing only about 1 to 2 per cent of arsenic, an amount small enough to insure its removal with the iron in the subsequent treatment.

The foregoing treatment of speiss worked very well, and if proper mechanical devices and fume-handling apparatus had been used would have been the best way to deal with it. The apparatus was quickly destroyed and the fume-collecting arrangements were entirely inadequate. Instead of curing these troubles, the scheme of sulphating and dissolving sulphate directly was adopted, as it was considered that the cheap blast-furnace smelting of the bulky muds would be the most feasible thing to do.

Upon long-continued boiling of the sulphates in water, by far the greater part of the nickel and cobalt was obtained in a neutral, practically iron-free solution, and the whole of the silver and the arsenic, and most of the iron in a mud, which contained about 72 per cent silver.

The solution of cobalt and nickel was treated with scrap iron to remove the very small amount of copper present, and then blown with air and soda ash added to get rid of the small amount of iron.

The iron-free solution was in part treated with soda ash to throw down "blue mud," a mixture of hydroxides of cobalt and nickel. The blue mud was washed to remove sulphates as far as possible and was then pulped in a solution of common salt and electrolyzed in a modified Haas-Oettel cell, using graphite plates. Each cell took about 100 amp. at about 60 to 90 volts, and peroxidized the metals very efficiently.

The mixture of nickelic and cobaltic hydroxides was separated from the brine and after washing was boiled with strong cobalt-nickel sulphate solution to get rid of the nickel. This reaction (Herrenschmidt's process) did not work well enough and it was always necessary to use some acid to reduce the nickel content to a passable amount.

Although it appears probable that the Herrenschmidt process may be made to work satisfactorily for the separation of the greater part of the cobalt from nickel, it has been impractical to make cobalt oxide with less than 2.5 per cent nickel, or nickel solutions with less than 1 cobalt to 5 or 6 nickel by this process.

The present cobalt processes retain most of the features mentioned above.

The two chief operating companies on this continent are the Deloro Smelting & Refining Co., Deloro, Ont., and the Coniagas Reduction Co., Ltd., Thorold, Ont. These smelters treat cobalt ores, concentrates, and residues from the silver mills at Cobalt, Ont.

**Present Practice.**—One of the processes at present used is briefly as follows: The ore is charged to the blast furnace and smelted with the necessary fuel and flux to form a speiss and to slag off gangue matter. Speiss is an artificial arsenide or antimonide. The speiss is ground and given an oxidizing roast, during which a large part of the arsenic (and antimony) is driven off. This is followed by a chloridizing roast with  $\text{NaCl}$ . The chloridized speiss is then charged into agitating tanks and the silver extracted by cyanide solution, from which it is recovered by precipitation with aluminum dust as metallic silver. In this process most of the cyanide is regenerated. The residue from the cyanide treatment is sulphated,

most of the iron, copper, arsenic, antimony, silver, cobalt, and nickel being thus made water soluble. The sulphated speiss is charged to agitation tanks containing water and the resulting pulp agitated. The iron, arsenic, and antimony are then precipitated from solution by means of ground limestone. The solution is then freed of copper by means of soda ash and the cobalt and nickel precipitated fractionally by means of alkaline hypochlorite solution. The cobalt and nickel "muds" are calcined to commercial oxides and sold as such or reduced to cobalt or nickel metal.

By another method at present being practiced the ore is not cyanided, but otherwise this process is much the same as that previously outlined. In this process the ores are smelted in the blast furnace to a speiss carrying the cobalt, nickel, and silver. This speiss is roasted to drive off arsenic and antimony. The roasted speiss is sulphated and the sulphated speiss dissolved in water. The treatment of the solutions is thenceforward much the same as that of the preceding method. The essential difference between the two processes is that by one the silver is recovered by cyaniding, by the other the silver is recovered in the precipitate obtained by neutralizing the slightly acid solution of the dissolved speiss. This precipitate, high in silver, is smelted in the blast furnace, producing a crude silver bullion which is refined electrolytically and shipped as bullion 999 fine.

**Blast-furnace Smelting of Cobalt Ores.**—The blast-furnace products may be classified as crude silver bullion, speiss, matte, and slag. These four products are given in the order of their specific gravities. The bullion is the heaviest and the slag the lightest. Fume and dust are also recovered and constitute with the gas the remaining products of the furnace.

Bullion, speiss, and matte are tapped from the crucible of the furnace into pots. The slag is also tapped into pots when it is desired to return it to the furnace, otherwise it is granulated. Gases, fume, and dust from the charge pass from the top of the furnace through a downcomer to flues, where most of the flue dust settles out, the fume being blown by a fan into the bag house, where crude arsenic is recovered. The bags are made of wool. They are shaken at intervals and the crude arsenic, contaminated with  $PbO$  and  $Sb_2O_3$ , falls into the arsenic cellars. Crude silver bullion is obtained as such in the speiss pots when the charge to the furnace is sufficiently rich in silver to saturate the speiss and matte and have silver left over to form bullion. By precipitation with metallic iron the speiss and matte can be rid of most of its silver, the iron replacing the silver. The silver collects in the bottom of the speiss pot and upon cooling separates easily from the solidified speiss. Lead and copper are the chief impurities in the crude bullion, but the impurities will depend upon the charge to the furnace. This bullion assays approximately 750 to 800 fine and, as has been mentioned, is brought up to market fineness by electrolytic refining.

Speiss is an artificial arsenide or antimonide. In the case of the cobalt ores its antimony content is usually negligible compared to its arsenic content. A typical analysis is:

Per cent						
Co	Ni	As	Fe	Cu	Sb	Ag
20	12	23	18	3	1	800 oz.



The charge must contain sufficient arsenic to combine with the cobalt and nickel. If there is not sufficient arsenic in the charge, or if too much of the arsenic is oxidized or volatilized and passes out in the fume, then cobalt and nickel will be slagged off.

The affinity for arsenic of nickel, cobalt, and iron is in the order given. Their affinity for oxygen is in the reverse order, hence iron will be oxidized in preference to cobalt, and cobalt in preference to nickel. It is necessary, therefore, to prevent oxidation of cobalt compounds, and to do this it is necessary to prevent too much oxidation of iron. The usual speiss made runs approximately 18 per cent iron and 23 per cent arsenic, but this will vary according to the extent of oxidation permissible in the charge. The ratio of iron to arsenic in the speiss is fixed within certain limits. It is desirable to have iron present in the speiss in such amounts that, when the speiss is roasted, the resulting calcine will have approximately a certain Fe:As ratio. The reason for this will be made clear later.

The speiss, therefore, should contain all the cobalt and nickel, together with the combining arsenic and the necessary iron. Matte as formed in the cobalt blast furnace always contains some arsenic. Some "mattes" that have been made approach more the nature of a speiss, as their arsenic contents have been nearly as high as their sulphur contents. They are called mattes, however, because the percentage of arsenic is, as a rule, very low, the metals being present mostly as sulphides, and also because "matte" forms a separate layer from speiss in the pots. The two are usually easily separable after the speiss pots are cooled. Mattes usually contain a higher ratio of cobalt to nickel than speiss formed at the same time. If the ratio of cobalt to nickel in the charge is 2:1, then the ratio of cobalt to nickel in the matte will usually be greater than 2:1, and in the speiss the ratio will be less than 2:1.

The usual practice is to form as little matte as possible, as it requires a different roasting treatment than speiss. It is impossible, however, to avoid forming some matte when sulphur is present in the charge. When matte is made in small amounts it is usual to mix it in with the speiss and treat it as speiss. This is not possible where large amounts of matte are made.

The matte contains considerable iron and silver. A typical matte will contain:

Per cent						
Co	Ni	As	Fe	Cu	S	Ag
9	4	5	27	12	23	2,000-7,000 oz.

It is impossible to effect a complete concentration in a matte or in a speiss of cobalt, nickel, iron, copper, or silver where matte and speiss are being formed at the same time in the furnace.

Limy charges tend to prevent the formation of speiss and to encourage the formation of matte. The use of too much limestone is on that account to be avoided.

**Slag.**—The usual slag is a bisilicate, alumina being considered neutral. The chief constituents are  $\text{SiO}_2$ ,  $\text{FeO}$ ,  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{MgO}$ . The slags vary, however, frequently, variations being caused chiefly by such ingredients as  $\text{PbO}$ ,  $\text{MgO}$ , and  $\text{ZnO}$ , which occasionally cause the slag to flow poorly. The silver loss in slag is kept around 3 to 4 oz. per ton and nickel plus cobalt under 1.00 per cent.

In calculating the slag it is necessary to allow for the iron required by the sulphur and arsenic to form matte and speiss, the remainder of the iron being, after oxidizing, available for slag. The extent of oxidation in the furnace will depend chiefly upon the coke and the air supplied. It is customary to use about 12 per cent coke on the charge, but this may be cut down to 10 per cent on charges in which there is sufficient heat developed by the oxidation of the As and Sb to  $\text{As}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$  and the S to  $\text{SO}_2$  to carry on the smelting operation.

It is frequently necessary to add return slag to the charge, especially where fines constitute a large portion of the charge. The coarse slag helps to keep the charge open and aids in melting it.

**Charging.**—The furnaces in operation at present are hand charged, the ore, fuel, and fluxes being brought to the feeding floor in wheelbarrows. The coke on each charge is fed in first. Hand feeding, when carefully done, helps to avoid caking in the furnace, which may easily occur when smelting the varied by-products of the plant. Fines have been briquetted, but no especial difficulty in smelting them has been experienced when they are not briquetted. The extra expense of briquetting may in some cases be worth the increased speed of smelting, but it is not general practice with cobalt concentrates or fine residues.

The blast furnace frequently has to handle on short notice large amounts of precipitates from the wet plant. These often contain as high as 40 per cent moisture and their nature is by no means homogeneous. As a result, it is frequently impossible to calculate a charge for the material being smelted and experience alone serves as a guide to the operation of the furnace.

**Fume.**—The fume from the arsenic cellars is heated in hand-fired reverberatory furnaces and  $\text{As}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$  sublime. The  $\text{Sb}_2\text{O}_3$  is separated in flues from the most of the  $\text{As}_2\text{O}_3$ , which passes through flues to the arsenic bag house, where it is obtained as 99 per cent  $\text{As}_2\text{O}_3$ . The unsublimed residue from the arsenic furnaces carries silver and considerable lead, together with small amounts of cobalt and nickel. It is returned to the blast furnace.

**Treatment of Speiss.**—The "raw" or "green" speiss from the blast furnace is crushed and ground and then roasted in Bruckner coal-fired roasters to eliminate arsenic and antimony. Complete elimination of these is not possible. The usual practice is to roast to about 10 per cent arsenic. A further reduction in the arsenic content of the calcine is possible by prolonged roasting or by the addition of a reducing agent, such as coal or coke. Roasted speiss may by such means be brought down to 3 and 4 per cent arsenic, but such practice is not commercially practicable.

The arsenic in the calcine is largely present as arsenite. When powerful basic substances are present, arsenites take up oxygen and become arsenates. When no free oxygen is present the arsenites decompose into arsenates and arsenic vapor.



When there is excess oxygen, high red heat, and absence of powerful basic substances, then the arsenite condition is the stable form and  $\text{As}_2\text{O}_3 \rightarrow \text{As}_2\text{O}_5 + \text{O}_2$ .

During the initial stages of roasting, the charge must not be heated up too rapidly, or it will stick to the sides of the furnace and will ball up considerably. When the temperature of the calcine is approximately  $400^\circ\text{C}$ . the charge becomes self-roasting and during this stage the external source of heat is removed. When the self-roasting

stage is over, the temperature is raised to approximately 850 to 900°C. until sufficient decarbenization has been accomplished. The calcine is then in the cyanide process given a chloridizing roast, during which a further reduction in the arsenic content of about 2 to 3 per cent takes place. If the roasted speiss is not to be cyanided it is reground and sulphated.

The gases and the fume from the roasters pass through a system of flues to a Cottrell treater. In the flues and treater practically all of the arsenic is recovered.

**Sulphating.**—The roasted speiss or residue from the cyanide treatment is mixed with concentrated sulphuric acid in a cast-iron pot and is stirred by paddles rotated from a central shaft. The mixture is of a soupy nature and when stirring is finished it must be run out of the mixer while still fluid, as when the sulphating action commences the speiss rapidly hardens. The amount of acid added is usually adjusted so that there will be sufficient acid present to convert all the metals to soluble sulphates. There is always a portion of the speiss not attacked by the acid and, therefore, this portion of the speiss is undissolved in the first dissolving process.

**Dissolving the Speiss.**—The sulphated speiss is charged into wooden tanks and agitated with water. Most of the copper, iron, cobalt, nickel, and arsenic are dissolved in this process. Antimony hydrolyzes rapidly and most of it precipitates as a very fine white precipitate. It is usual to have a certain amount of free acid present in the solution, and this is neutralized by the addition of calcium carbonate. On neutralizing the acid, most of the arsenic, antimony, and some iron are precipitated as iron arsenate, antimoniate, arsenite, and antimonite. The precipitate formed carries down with it the hydrolyzed antimony precipitate and also the silver and the insoluble portion of the speiss. The solution is pumped through presses and the mud is returned to the blast furnace.

This mud carries practically all the silver in the speiss and where the silver has not been previously extracted by cyanidation this mud acts as collector for the silver and is smelted in a similar manner to a high-grade silver concentrate yielding a crude silver bullion when smelted in the furnace.

**Precipitation of Iron.**—The solution is then freed of iron and arsenic by precipitating the iron with calcium carbonate. The last traces of arsenic are brought down with the iron and the solution is then sent to the copper tanks for elimination of the copper. To insure the removal of all the arsenic it is usual to have sufficient iron in the speiss solution to combine with the arsenic to form ferric arsenate ( $\text{FeAsO}_4$ ), i.e., 56 of iron to 75 of arsenic. It is customary to allow a margin of safety, so that the iron may be to the arsenic in solution as high as 2 or 3:1. This is why it is always necessary to have a certain ratio between the arsenic and the iron in the original green speiss. Where the speiss is high in copper, this ratio may be somewhat lessened, and may be as low as 1.5:1, as copper aids in the precipitation of arsenic. The iron mud is usually a waste product.

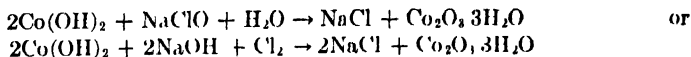
**Precipitation of Copper.**—To the solution from the iron tanks sodium carbonate is added. This precipitates all the copper as a basic carbonate. When the ratio of cobalt plus nickel to copper in the solution is high, some cobalt and nickel will be brought down with the copper. This copper mud is dissolved in  $\text{H}_2\text{SO}_4$  and sent to the bluestone plant. Here it is crystallized as copper sulphate. The mother liquor, enriched in cobalt and nickel, is returned to the system in the cobalt plant.

In the crystallization of copper sulphate from a solution containing cobalt and nickel, the first or crude crystals are formed from a solution whose original specific gravity as delivered to crystallizing tanks is approximately 1.40. The solutions contain varying concentrations of copper, cobalt, and nickel. The first crystals will form uncontaminated with cobalt or nickel until the concentration of cobalt and nickel is great enough to cause the formation of a dark-colored crystal on top of the blue copper crystals. The dark crystals are a double sulphate of cobalt and nickel. When these crystals commence to appear, the mother liquor is pumped back to the cobalt house and the crystals removed, washed, and later redissolved and recrystallized. The bluestone plant provides one method of disposing of the copper. At the Missouri Cobalt Co., copper was removed from solution by electrodeposition previous to the elimination of iron in the cobalt plant. Copper may also be precipitated by scrap iron or may, as at Maletre & Co., France, be precipitated by  $H_2S$ , the solution being boiled after filtering to drive off  $H_2S$ .

**Manganese.**—This is not present in very great amounts in Canadian ores, but in the smelting of New Caledonia ores it had to be eliminated. It was customary to precipitate cobalt and nickel from a solution containing cobalt, nickel, and manganese by means of sodium sulphide, the manganese remaining in solution.

**Precipitation of Cobalt.**—Cobalt is precipitated from the sulphate solution after copper has been removed. The precipitants are alkaline hypochlorites, usually a solution of  $NaOCl$  made by passing chlorine gas into a solution of  $NaOH$  and  $Na_2CO_3$ . It was formerly the practice to use  $CaOCl_2$  (bleaching powder) in the manufacture of the sodium hypochlorite. The use of liquid chlorine as developed at the Comagac Reduction Co. possesses several obvious advantages over this former method. Were  $CaOCl$  used as an emulsion the  $CaO$  of the bleach would form insoluble calcium sulphate when sulphate solutions are being treated. This would have to be washed out of the precipitate by means of hot  $Na_2CO_3$  solution and would entail unnecessary trouble.

The precipitation of cobalt from a sulphate solution by alkaline hypochlorite solution is obtained by a rather complicated reaction. Upon the addition of the bleach, the first reaction taking place is apparently the precipitation of a basic carbonate of cobalt of the composition  $x Co_2CO_3 \cdot y Co(OH)_2 + H_2O$ . The subsequent reaction is probably



The cobaltic oxide ( $Co_2O_3$ ) undergoes rapid alternate reduction and oxidation in the presence of hypochlorite. It, therefore, acts as a catalytic agent and promotes rapid evolution of oxygen from a continuous stream of bleach solution.

It is probable that not all of the  $Cl$  of the bleach forms  $NaCl$ , but that a certain amount of free  $HCl$  and  $Cl$  is liberated. The amount of  $Cl$  liberated is small. The amount of  $HCl$  formed is sometimes considerable, and some of this immediately reacts with the  $CoCO_3$  of the basic precipitate, evolving  $CO_2$  and forming  $CoCl_2$ , from which cobalt is again precipitated by fresh bleach solution, which is kept running into the tanks in a small stream during the process of precipitation.

The precipitation is stopped when nickel commences to come down with the cobalt. This will occur according to the ratio of nickel to cobalt in solution. Solutions with a ratio of 2  $Co$  to 1  $Ni$  may be carried much farther in the precipitation of nickel-free cobalt than solutions where the  $Co$  to  $Ni$  ratio is as 1.1.

As it is desired to make an oxide with under 1 per cent nickel, it is usual to keep the nickel in the "mud" under 0.6 per cent nickel, consequently, when the cobalt precipitate begins to be contaminated with nickel, precipitation is stopped and the pulp pumped through a press. The color of the solution is used as a guide in the progress of the cobalt precipitation. When solutions of cobalt and nickel sulphates are mixed, various colors result according to the concentration of the two in solution. It is usual to adopt a standard solution as a colorimetric standard for the guide of operators. When the solution in the cobalt tank reaches the required color, then the precipitation is stopped. The color of cobalt sulphate solution is rose red, that of nickel sulphate is green. A mixture of cobalt and nickel sulphates in the ratio of approximately 2 Ni: 1 Co is, if the solution is fairly dilute, practically colorless. It will be seen then that a variety of shades is obtainable by merely altering the concentration of either the cobalt or the nickel.

The "mud" from the cobalt tanks is a dark-brown color. It contains, when dry, approximately 59.0 per cent cobalt. It is calcined with soda ash to split up basic sulphates of cobalt and the calcine washed and dried or given a roast to bring the cobalt content to that required in the oxide for shipment. Black oxide approximates 71 per cent cobalt plus nickel. The nickel is usually under 1 per cent. Gray oxide is obtained from the hydrated oxide in a similar manner to the black oxide. It is given a longer and hotter final calcine than the black. This raises the cobalt content to 75 to 76 per cent cobalt. The oxide is pulverized and shipped as black or gray oxide. The gray oxide may also be reduced to metal.

**Precipitation of Cobalt and Nickel.**—The solution from the cobalt tanks is sent to the intermediate tanks. Here the last traces of cobalt are precipitated by the further addition of bleach solution. Some nickel comes down with the cobalt. The ratio of cobalt to nickel in a typical intermediate mud is approximately 9 of Co: 1 of Ni. The ratio of Co: Ni in solution previous to the precipitation of the intermediate mud is approximately 2:3. The intermediate mud is redissolved and returned to the system.

**Precipitation of Nickel.**—The solution from the intermediate tanks, after being freed of cobalt, contains approximately 5 to 8 g. per liter of nickel, together with considerable NaCl,  $MgSO_4$ , and  $Na_2SO_4$ . The NaCl is formed during the bleach reaction. The  $Na_2SO_4$  is formed in the copper tanks and the  $MgSO_4$  is formed when dolomitic limestones are used as precipitants or neutralizing agents in the first part of the wet process.

The nickel is precipitated by soda ash as a basic carbonate of a similar nature to the cobalt precipitate. When the concentration ratio of magnesium sulphate to nickel sulphate becomes high enough, a basic magnesium carbonate will be precipitated. Consequently, when the solutions carry considerable  $MgSO_4$  it is impracticable to precipitate all the nickel from solution, as increasing amounts of magnesium carbonate will be brought down with it. Moreover, the solutions at this final stage in the process have become nearly saturated with respect to NaCl and  $Na_2SO_4$  at the usual solution temperatures, so that further addition of  $Na_2CO_3$  causes separation of  $Na_2SO_4$  and some NaCl.

The precipitation of nickel by  $Na_2CO_3$  will give good results until about 85 per cent of the nickel is precipitated. A small amount of bleach solution is then added, and thus a further 10 to 14 per cent of the nickel is precipitated. It will not always be economical to attempt to precipitate over 95 per cent of the total nickel in solution.

The hydrated nickel oxide is black in color. It contains approximately 45 per cent nickel on a dry basis, and is usually contaminated with small amounts of  $Na_2SO_4$ .

and NaCl. It is calcined to the green oxide (NiO) and shipped as such or reduced to metal.

**Reduction of Cobalt and Nickel Oxides to Metal.**—The reduction is carried out in electric furnaces as a rule. A usual type is the three-phase, Heroult tilting furnace. The oxide is reduced by carbon furnished by charcoal and coke in the charge and partly by the electrodes.  $\text{CaCO}_3$  is added to slag off sulphur. The metal is shotted and shipped in barrels. The carbon approximates 1.0 per cent; the sulphur 0.015 per cent.

Kalmus has experimented on the preparation of metallic cobalt by the reduction of the oxide. He used as reducing agents carbon, hydrogen, cobalt and aluminum. His results are useful to those interested in the production of a pure cobalt metal carbon- and sulphur-free.<sup>1</sup>

**Physical Properties of Metallic Cobalt.**—Metallic cobalt resembles nickel in general appearance. Cobalt has a slight bluish cast that nickel has not. Brinell hardness is 119.1, tensile strength varies from 63,500 to 34,410 lb. per square inch according to its treatment in casting, annealing, and working. The pure metal can be readily machined, it is magnetic up to 1100°C. approximately. Its density is 8.79 to 8.93 and it melts at about 1444°C.<sup>2</sup>

**Chemical Properties.**—Cobalt is soluble in most dilute acids. It dissolves slowly in all but nitric, with which it reacts readily. It forms cobaltous and cobaltic salts. Cobaltous salts are but little hydrolyzed but the cobaltic salts are decomposed by water, liberating readily one-third of the negative radical. Complex cations and anions containing cobalt are very numerous and stable, especially cobalt amines. Most cobaltous compounds are red when hydrated or in dilute solution and blue when dehydrated or in concentrated acid solution.

Alkaline carbonates precipitate a basic carbonate from cobalt solutions, soluble in concentrated solutions of the same carbonate. Potassium nitrite produces in solutions of cobalt salts in the presence of acetic acid a precipitate of yellow potassium cobaltic nitrite. This reaction is frequently used in plant practice as a control test to detect cobalt in the presence of nickel.

The usual analytical method of estimating cobalt in ores and smelter products is the electrolytic assay. Cobalt and nickel are plated out of an alkaline solution, the deposit weighed, the nickel in the deposit obtained by the dimethylglyoxime method and the cobalt obtained by difference.

Nitroso- $\beta$ -naphthol is also used to determine small amounts of cobalt in the presence of nickel.

It may be of some interest to know that cobalt oxide is precipitated from an alkaline cobalt solution by grape sugar in a similar manner to the reduction of copper salts to CuO by Fehlings reaction.

**Commercial Uses of the Metal.**—Cobalt oxide is used chiefly in the ceramic industries as a coloring agent. It is also used in the paint and color industries. Cobalt oxide is used in the enameling of sheet iron, as it aids the enamel to adhere to the sheet iron.

Considerable cobalt metal is used in the production of "Stellite," a high-speed tool steel. Stellite is a cobalt-chromium alloy. It does not lose its hardness even when the cutting edge is red hot, and therefore possesses considerable advantages over

<sup>1</sup> Canadian Dept. of Mines, *Bull.* 259

<sup>2</sup> The above data and considerable other information on the physical properties may be obtained from KALMUS and HARPER, Canadian Dept. of Mines, *Bull.* 309.

ordinary high-speed tool steel. Electroplating with cobalt has been investigated by Kalmus.<sup>1</sup> He found cobalt to plate much more efficiently from solution than nickel and the platings produced withstood the usual tests to which nickel plate is subjected.<sup>2</sup>

The use of cobalt metal in magnetic steel is becoming more and more popular, and may in the future have a considerable bearing in the manufacture of lifting magnets and of magnetos.

<sup>1</sup> Canadian Dept of Mines, *Bull* 334

<sup>2</sup> Alloys of cobalt are discussed at some length by Drury (*Rept*, Ontario Bureau of Mines (1918) 27, Part 3, Sec 1).

## CHAPTER XXXIX

### NICKEL

By A. J. WADHAMS<sup>1</sup>

**Ores and Deposits.**—Nickel ores are of widespread occurrence throughout the world. They are found in almost every country of Europe, in Africa, India, China, South America, Cuba, and in various localities in the United States. The most important deposits, however, occur in Canada, New Caledonia, and Norway. Compared with the other two, the Norwegian deposits are relatively small, but were important during the World War, when all their production went to Germany at high prices. During the height of their prosperity, nearly 80,000 metric tons of ore containing approximately 1.20 per cent nickel and 0.50 per cent copper were treated per year.<sup>2</sup> The ore is similar in character to the principal Canadian deposits, but is of lower grade.

The existence of nickel ore in New Caledonia has been known since 1865, and the deposits have been worked since 1875. From the latter date until the end of 1915, about 2,245,354 metric tons of ore were exported.<sup>3</sup> Additional ore smelted on the island produced 26,368 tons of matte, containing about 45 per cent nickel. It is estimated that the contents of the ore and matte amounted to 156,394 tons of metallic nickel. During recent years the tonnage produced has declined rapidly. In 1916 it was 35,614 metric tons and in 1917, 32,017 tons.<sup>4</sup> These figures include the ore smelted on the island. Previous to 1881 the ores produced contained from 10 to 12 per cent nickel, but since that time the grade has been steadily falling off until now it is about 5 per cent. The New Caledonia ores consist principally of *noumeaite* or *garnierite*, a hydrated nickel-magnesium silicate, to which the formula  $(\text{NiMg})\text{SiO}_2 \cdot \text{H}_2\text{O}$  has been assigned. The ore, as mined, contains 20 per cent or more of hygroscopic moisture, besides about 10 per cent combined water, and is dried before shipping. The following analysis is representative of the composition of the ore as shipped: Ni, 5.0 to 6.0;  $\text{SiO}_2$ , 48.0; Fe, 14.0;  $\text{MgO}$ , 15.1; and combined  $\text{H}_2\text{O}$ , 10 per cent. A more complete analysis representing an average of the 7 per cent ore after drying at  $100^\circ\text{C}$ . is as follows:<sup>5</sup>

	PER CENT
$\text{SiO}_2$ .....	42.0
$\text{MgO}$ .....	22.00
$\text{CaO}$ .....	0.10
$\text{Al}_2\text{O}_3$ .....	1.00
$\text{Fe}_2\text{O}_3$ .....	15.00
$\text{NiO}$ .....	0.00
$\text{CoO}$ .....	0.15
$\text{MnO}_2$ .....	0.70
$\text{H}_2\text{O}$ .....	10.00
	<hr/> 99.95

<sup>1</sup> Manager, Development and Research Department, the International Nickel Co., New York, N. Y.

<sup>2</sup> "Mineral Industry," p. 887, 1918.

<sup>3</sup> Report Royal Ontario Nickel Commission.

<sup>4</sup> "Mineral Industry," p. 862, 1918.

<sup>5</sup> Report Royal Ontario Nickel Commission, p. 247.



The absence of copper and sulphur is particularly noteworthy. The Canadian ores contain both, and to this fact is due the different methods of smelting and refining used. There is no information available as to whether or not the New Caledonia ore contains any of the precious metals. In any event, none are recovered.

The New Caledonia deposits of nickel are associated with a very basic rock which is now largely altered into serpentine. The nickel mineral is found in small veins in the serpentine and as concretions enclosing undecomposed rock masses. The garnierite is an alteration product, in which the nickel replaces the magnesia of the serpentine. When pure, the color is green, but the presence of iron causes a wide variation, passing through yellow and brown to almost black. The deposits are always found in the form of shallow beds on the slopes of spurs from the main mountain range of the island, and at elevations of from 400 to 2,500 ft. The beds are seldom more than 15 or 20 ft. thick by half a mile in length and are relatively narrow. There is often a heavy overburden of soil or clay, which adds to the difficulty of working. As a rule, the individual deposits do not exceed 100,000 tons, though one mine produced 600,000 metric tons.

By far the most important deposits of nickel known at the present day are those of the Sudbury district, Ont., Canada. Nickel ores have been discovered at a number of points in Canada, but from two only, besides the deposits of the principal district, has there been any production. These are the Alexo mine on the Temiskaming & Northern Ontario Ry., near Matheson, Ont., which shipped ore for a number of years to the Mond Nickel Co.'s smelter at Coniston, and the Cobalt silver district, where nickel, chiefly in the mineral niccolite, is found associated with the silver, and is recovered as a by-product at the various plants where the silver bullion is produced. The Alexo mine has not been in operation since 1921.

The ores are closely associated with a pre-Cambrian intrusion of noritemicropegmatite rock, which encloses an oval-shaped area of later sedimentary rocks. The longer axis of the oval lies in a northeasterly, southwesterly direction and is about 33 miles in length. The width is about 13 miles. The enclosing norite ring, which is acid in character towards the inner part and shades to a basic composition as it approaches the outer edge, has a varying width of from 2 to 4 miles. Most of the known deposits are found at the outer or basic edge of the norite, but some important ore bodies known as offset deposits have been worked at a distance of several miles from the basic edge. There are a number of theories regarding the origin of the ore. The view advanced by Dr. A. P. Coleman, that the deposits were due to a magmatic segregation of the sulphides from the norite, was widely accepted at one time, but there have been many serious objections to it made by subsequent investigators. A more recent theory is that there has been an injection of sulphides at a period later than the intrusion of the norite, and it is also believed by many that the action of water has been an important factor in at least some, if not all, of the deposits.

The ore consists mainly of magnetic iron pyrites, or pyrrhotite, always mixed with more or less rocky matter or gangue, but often remarkably free from it and then massive and close grained in appearance. Various formulas have been worked out for the pyrrhotite, but, on the whole, it corresponds very closely to  $\text{Fe}_9\text{S}_8$ . Copper, in the form of chalcopyrite, ( $\text{CuFeS}_2$ ), is always present, frequently in sufficient quantity to be easily distinguishable by the eye. The nickel mineral, however, is so intimately associated with the pyrrhotite that, in general, nothing short of a chemical analysis will establish its presence. By the use of a magnet on the finely ground ore from selected specimens free from copper, and by the exercise of a good deal of patience, it is possible to separate the ore into a magnetic and a non-magnetic portion. The former will consist of barren pyrrhotite, while the latter will be the nickel-bearing mineral. Careful work of this kind has shown the nickel mineral to be pentlandite<sup>1</sup> ( $(\text{NiFe})_{11}\text{S}_{10}$ ),

<sup>1</sup> Dr. C. W. Dickson.

containing Ni 36.0 per cent, Fe 30.4 per cent, and S. 33.6 per cent. Another nickel mineral, polydymite ( $\text{Ni}_2\text{FeS}_4$ ), is met with in some of the mines in readily distinguishable masses, but, although such occurrences are very rich in nickel, polydymite is of secondary economic importance. Of interest only mineralogically are such minerals as millerite ( $\text{NiS}$ ), niccolite ( $\text{NiAs}$ ), and gersdorffite ( $\text{NiAsS}$ ) which are found occasionally. The following analyses will give an idea of the character of the ore from the various mines which are now operating, or have recently been in operation:

Mine	Per cent	
	Cu	Ni
Frood <sup>1</sup>	1 50	1 68
Creighton <sup>1</sup>	1 56	4 43
Crean Hill <sup>1</sup>	2 91	2 14
Garson <sup>1</sup>	1 90	2 30
Worthington <sup>1</sup>	3 40	3 00
Levack <sup>1</sup>	0 50	2 80
Victoria <sup>1</sup>	3 40	1 90
Murray <sup>2</sup>	0 95	1 85
Whistle <sup>2</sup>	0 10	2 76

<sup>1</sup> Report Royal Ontario Nickel Commission

<sup>2</sup> COLMAN, A. P., "Nickel Industry"

With the exception of the last two, the figures are averages over a number of years.

All ores mined contain, in addition to the copper and nickel values, small amounts of the platinum-group metals, as well as a little gold and silver. These metals are concentrated during the smelting operations and are collected in the matte which goes to the refining process. No reliable analyses are available of the precious-metal content of the ores, but the following analyses<sup>1</sup> of two samples of converter matte, 1 ton of which represents from 15 to 25 tons of ore, indicate that the amounts present in the ores are small

	Ounces per ton	
	No 1	No 2
Gold	0 027	0 256
Silver	1 840	6 155
Platinum	0 1235	0 988
Palladium	0 197	0 984
Iridium	0 016	0 065

Though the amount of the precious metals in the ores is not large, their recovery from the matte brings an appreciable quantity into the market.

The gangue rock associated with the ore is, in general, of two kinds, acid and basic, with the latter predominating. The acid rock is mainly granite from the foot wall. The norite forms the hanging wall and some is found mixed through the ore, as is also

<sup>1</sup> Report Royal Ontario Nickel Commission.

an associated greenstone. The following analyses<sup>1</sup> are the averages of a number made on each kind of rock:

	Per cent	
	Acid	Basic
SiO <sub>2</sub>	67 862	52 770
Al <sub>2</sub> O <sub>3</sub>	12 688	18 943
Fe <sub>2</sub> O <sub>3</sub>	1 740	0 283
FeO	5 072	9 140
MgO	1 164	4 940
CaO	2 468	7 617
Na <sub>2</sub> O	3 956	2 597
K <sub>2</sub> O	2 780	1 330
H <sub>2</sub> O	1 050	1 263
TiO <sub>2</sub>	0 456	1 097
P <sub>2</sub> O <sub>5</sub>	0 178	1 300
MnO	0 036	
	99 452	99 760
Specific gravity	2 718	2 897

The ore as shipped from the mine seldom contains less than 30 per cent rock, and may have 50 per cent or more.

From the time of the discovery of the Sudbury deposits to the end of 1916, there was smelted a total of 10,322,515 tons of ore, which produced 284,538 tons of nickel and 175,003 tons of copper, showing an average recovery of 1 695 per cent copper and 2 759 per cent nickel. The following table gives the production and metallic contents of the ore mined and smelted during the past six years.

	Tons				
	Ore mined	Ore smelted	Copper in bessemer matte	Nickel in bessemer matte	Bessemer matte
1917 <sup>1</sup>	1,518,783	1,453,661	21,196	41,887	78,897
1918 <sup>1</sup>	1,641,617	1,559,892	23,482	45,886	87,184
1919 <sup>1</sup>	572,400	754,567	12,099	22,035	42,736
1920 <sup>1</sup>	1,135,792	1,086,159	16,000	30,557	57,938
1921 <sup>1</sup>	257,154	393,768	6,323	9,628	19,497
1922 <sup>2</sup>	259,569	314,120	5,421	8,677	17,324

<sup>1</sup> The Mineral Production of Canada 1921

<sup>2</sup> Dominion Bureau of Statistics, Dept. Mines, Ottawa

The figures show clearly the effect of the close of the war on production. In the past, the nickel went largely into armaments, but the diversified uses which are now being found for it are again rapidly building up the industry.

<sup>1</sup> COLEMAN, A. P. "The Nickel Industry"

## MINING METHODS

**New Caledonia Ores.**—Owing to the great difference in the nature of the deposits which form the two principal sources of the metal, the methods of mining are widely different. T. P. Sutherland, Chief Inspector of Mines for Ontario, describes the mining practice in New-Caledonia as follows

Where surface indications of ore are found, prospecting pits are dug into the hillside, and, if a good grade of ore is discovered, without too great an overburden, a series of pits are dug across the slope to define the extent of the ore occurrence.

If the overburden is over 9 ft in thickness and the grade of ore below 5 per cent of nickel, the prospect is not considered favorably. If the preliminary work shows an ore occurrence of sufficient tonnage and grade to be profitably worked, 25-ft contour lines are run along the hillside. These lines are graded out and are called levels. Tracks are laid and mining commences. The overburden for a few feet back is removed, loaded into cars and trammed to the dump. The ore is then picked or barred down and carefully sorted. The shell of ore around the boulders or blocks of serpentine is picked off, the waste trammed to the dump, and the ore carefully gathered into piles and sampled. This procedure is repeated until the face becomes too low grade to pay. Occasionally, it is necessary to drill and blast the harder portions of the serpentine, and for this work hand steel is used. Large blocks of low-grade ore or waste are worked around and left standing on the bench. The ore is gathered from the different levels into a central loading station and transported from the mine to the foot of the mountains by aerial tram.

One noticeable feature of the nickel mining in New Caledonia is the extreme care used in sorting and sampling the ore. After the overburden is removed, the floor of the quarry is swept clean before the ore is picked or barred down. Then any large pieces of ore are broken by hammers to a 2-in. ring and carefully sorted by hand. In some cases, the fines are screened. The shell of ore on the boulders of undecomposed serpentine is chipped off as completely as possible with sharp picks, the waste is trammed to the dump, and the ore swept up and gathered into 10-ton lots which are carefully sampled. The result of the assay is marked on each lot. In this way ore of a certain grade can be shipped. The necessity for this extreme care is due to the fact that the ore is not uniform in grade, that it is impossible to judge closely the grade of the ore by appearance, and that in the past it has not been considered economical to smelt ore of a lower grade than 4.5 per cent nor to ship ore of a much lower grade than 6.5 per cent. The average content in nickel of the ore shipped in the three years 1913, 1914, 1915 was between 6.0 and 6.25 per cent, some shipments being above and others below this percentage.

**Smelting of New Caledonia Ores.**—The recovery of the nickel from the New Caledonia ores, which contain no copper, sulphur, or other element which might be expected to add to the difficulty of treatment, would, at first glance, appear to be quite a simple matter. The method of treatment originally proposed was to mix the ore with limestone to flux the siliceous gangue, and smelt the mixture with sufficient coke to reduce the nickel and furnish the necessary heat to produce liquid slag. The removal of the gangue as a molten slag could be accomplished readily enough, but the reduced metal or "fonte," containing about 65 per cent nickel along with considerable iron, proved difficult to deal with. It could not be bessemerized directly while still liquid, nor could it easily be broken up for further treatment after it had solidified. Moreover, as the coke used always contained a certain amount of sulphur, and as this was taken up with avidity by

the reduced nickel, it precluded the use of the "fonte" directly as ferronickel. The absence of the sulphur in the original ore proved to be only an apparent, and not a real, advantage. When these facts came to be recognized, the method now in use was adopted.

The present treatment is based on the production of a matte by adding suitable fluxes and sulphur-bearing material of some kind. Gypsum is the usual source of the sulphur, but alkali waste, chiefly calcium sulphide, or even pyrite, may be used. It is customary to briquette the ores with the necessary fluxes and any flue dust that is recovered. The briquettes,<sup>1</sup> after air drying, are smelted with 33 per cent coke in water-jacketed furnaces, producing a matte containing between 30 and 45 per cent nickel, and a slag assaying 0.30 to 0.40 per cent nickel. The furnaces originally used had a capacity of only about 20 tons per day, but the larger ones now operated have a capacity of 100 to 120 tons per 24 hr. The following analyses give the composition of the furnace charge and the resultant slag.<sup>2</sup>

	Per cent							
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	FeO	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	SO <sub>3</sub>	H <sub>2</sub> O
Ore	41 50			9 19	20 22	..	.	8 11
Briquettes	37 40	3 5		11 15	18 20	3 5	5.7	10 12
Slag	45 50	8 12	10 12		17 22	9 14		

The matte produced in the smelting operation is bessemerized in small converters, a siliceous flux being added to slag off the iron oxide formed. The product from the converters contains approximately 80 per cent nickel and 20 per cent sulphur, with the iron usually not over 0.25 per cent. It is next ground in ball mills to pass through 60 mesh and then roasted till free from sulphur, giving practically pure nickel oxide, which may then be reduced to metal by means of carbon or other reducing agent. The nickel oxide and the reducing agent are ground together and briquetted into either "rondelles," circular discs about 2 in. in diameter, and 1½ in. thick, or ¾-in. cubes, to meet the requirements of the market. The reduction is carried out by heating in horizontal retorts to bright redness for about 48 hr. The rondelles or cubes, when ready for the market, contain about 99.25 per cent nickel.

**Canadian Ores—Creighton Mine.**—The ore body is oval to narrow lenticular in shape, and is not sharply defined against the country rocks. The greatest extension, 2500 ft., so far developed is along the dip, which is about 45°. The level length varies from 1,000 to 800 ft., and the horizontal width reaches a maximum of 375 ft., with an average of over 100 ft.

The outline of the ore body was roughly determined by diamond drilling and divided transversely into alternate stopes and rib pillars extending from the footwall to the hanging wall, 60 ft. wide and 15 ft. wide, respectively.

The ore is crushed in the mine in 30- by 42-in. jaw crushers set at 6 in. and falls from the crushers into ore pockets, from which it is loaded into skips having a capacity of 9 tons, and hoisted to the rock house.

<sup>1</sup> GOWLAND, "Non-ferrous Metallurgy"

<sup>2</sup> Report Royal Ontario Nickel Commission.

In the rock house the ore is sized by three sets of trommels, the first set having screens with 6-in., the second 2½-in., and the third ¾-in. round holes. The oversize from these screens is coarse ore. The oversize from the first two sets of screens is hand sorted on sorting belts and the waste discarded. The sorted ore from the first trommel is recrushed to about 6 in. diameter in 48- by 15-in. crushers. The undersize from the third set is fines and falls directly into the fines bin. The waste sorted out amounts to about 15 per cent, and the fines to about 32 per cent of the total hoist.

**Murray Mine—British-American Nickel Corporation.**—The ore body is narrow lenticular in shape and extends to a depth of at least 2,000 ft., measured along the dip, which averages 36 deg. The level length averages about 1,200 ft., and the ore body is from 50 to 60 ft. in thickness measured at right angles to the strike and dip.

A modified room-and-pillar method of mining is used, with rooms 20 ft. wide and pillars 15 ft. wide. Raises 20 ft. high and 10 ft. wide, spaced on 35-ft. centers, are driven from level to level along the footwall contact. From each of the footwall raises between any two levels, three raises inclined 40 deg. are driven to the hanging wall. The first of these begins at the top of the box hole and is used as a blasting chamber when drawing ore and as a drilling place when taking out the inclined pillar which is left to protect the haulage drifts.

The distance from the center of the first raise to the center of the second is 25 ft., and from the second to the third raise is 50 ft. The ore between the upper two raises is stoped by machines set up in the raises. In the rock house it is crushed, screened, and about 10 per cent of waste is sorted out.

**The Garson Mine—Mond Nickel Co.**—The ore body is lenticular in shape and forms, roughly, an arc of a circle. The greatest length is about 1,000 ft. and the greatest width a little more than 100 ft. The dip is about 60 deg. and the proved depth is 1,800 ft. measured along the dip.

The ore body has been developed by means of drifts and section cutting until it is outlined on that level. Afterwards the workable portion, as shown by the assay plan, is mined, the poorer portions being left for pillars, if any are considered necessary.

Mill holes are cut in the solid and a portion of the back left over them for protection. Shoveling platforms are used for loading into the tram cars.

The stopes are filled with rock as the ore is removed. In the rock house the ore is crushed and sorted, about 25 per cent waste being discarded.

**Levack Mine—Mond Nickel Co.**—The ore body is lenticular and has a length of 500 ft. or more, and a maximum width, measured horizontally, of 150 ft. It extends to a depth of at least 3,000 ft., measured along the dip. The shaft, inclined 65 deg., is in a fold in the footwall, which extends well into the ore body. The levels are at 100-ft. vertical intervals.

Stoping is done by shrinkage stoping methods, keeping the back of the stope at such an angle that only wet holes are drilled. Both chutes and shoveling platforms are used.

In the rock house coarse waste is sorted out as the ore is conveyed from the storage bins to the crusher. After the ore is crushed, it is screened, and waste is sorted from the oversize from the screens. A total of about 33 per cent waste is sorted out.

**Smelting Methods—Canadian Ores.**—There are at present two operating companies treating ores from the Sudbury nickel field. They are the Inter-

national Nickel Co. of Canada, Ltd., and the Mond Nickel Co., Ltd. The smelters are located, respectively, at Copper Cliff and Coniston, both in the Sudbury district. In general, the treatment at the smelters, as distinguished from the refineries of the two companies, is identical in principle. Each company smelts its ore to a low-grade matte, which is then blown in basic converters for the removal of iron, producing a so-called "converter" or "bessemer" matte, which is shipped for subsequent treatment to the refineries situated, respectively, at Port Colborne, Ont.; and Clydach, Wales. The converter matte usually contains a small amount of siliceous matter, which, however, is not likely to exceed 0.10 or 0.20 per cent. It is customary to report any cobalt present as part of the nickel percentage. When determined separately, it does not usually exceed 0.30 or 0.40 per cent

Any precious metals originally in the ore will, of course, be found concentrated in the matte. The following are characteristic analyses of the matte sent to the refineries:

	Per cent				
Cu	25 04	24 09	30 20	39 10	29 50
Ni	56 58	55 17	(nickel plus cobalt)		
Co	0 57	0 36	52 20	46 25	53 80
Fe	0 14	0 18	0 16	0 21	0 19
S	17 93	19 80	17 00	14 25	16 35
	-	-	-	-	-
	99 26	99 90	99 56	99 81	99 84

Although, as stated before, the method of producing converter matte does not differ in principle at the two smelters, there is considerable variation in the details of operations. Both use water-jacketed blast furnaces and Peirce-Smith basic converters, though the designs and the sizes in each case differ widely. In addition, the International Nickel Co. still practices heap roasting for part of the coarse ore, and uses Wedge mechanical roasters and a reverberatory furnace for treating the fine ore. At Coniston the Mond Nickel Co. has abandoned the heap roasting that was once practiced there and sinters the fine ore and flue dust, as well as some flotation concentrates obtained from a portion of the ore, on Dwight-Lloyd sintering machines. The coarse green ore and the product from the sintering machines are smelted together in the blast furnaces. Some of these variations in the methods of treatment are to be attributed to difference in the character of the ores, while others are due to difference of opinion or to the inertia of established practice. Modifications in practice, however, are constantly being made. The International Nickel Co. is now (1923) experimenting with the sintering of the calcines from the Wedge roasters. The Mond Nickel Co. is doubling the capacity of its sintering plant and is putting in converters of a larger size.

**The International Nickel Co.**<sup>1</sup>—The ore, before being delivered to the smelter, is crushed at the mine to a maximum of 6 in., and then screened through trommels having circular openings  $\frac{3}{4}$  in. in diameter. The portion passing through the

<sup>1</sup> The information regarding this company is obtained largely from the *Report of the Royal Ontario Nickel Commission* and from a paper read at the March, 1920, meeting of the Canadian Institute of Mining and Metallurgy, on the "Mining and Smelting Operations of the International Nickel Co. of Canada, Ltd."

screens is known as "fines," in which the maximum-sized pieces are about  $\frac{3}{4}$  in. in greatest dimension, with the bulk of it much smaller. The oversize is called "coarse" ore. All production at the present is from the Creighton mine. Many attempts have been made to smelt this ore pyritically, but so far without success, and it is still necessary to roast a large part of it in order to obtain the grade of matte desired.

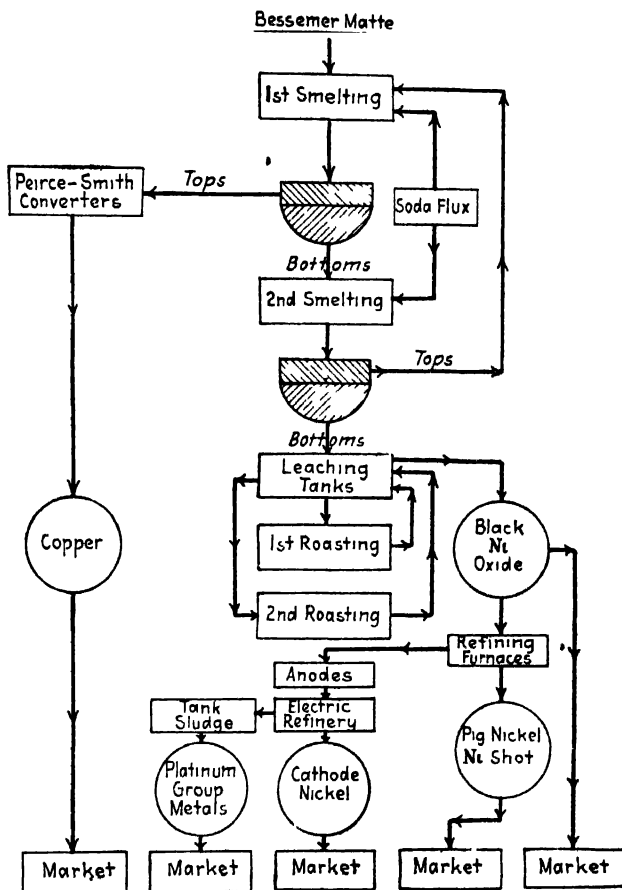


FIG. 1 —International Nickel Co's refining flow sheet (See p. 1301)

**Roast Yard.**—The roast yard is located about 4 miles from the mine and 11 miles from the smelter, in a tract of country where the fumes can do little damage. The ore is shipped from the mine in standard-gage, bottom-discharge, 50-ton steel cars, and when received at the roast yard is dropped into sunken pockets below the tracks, from which it is mechanically elevated into specially designed 100-ton steel cars, which can be completely discharged through a series of thirteen gates along one side. The 100-ton cars are now taken to the roast yard proper and spotted at the ore bridge, which is used to build the beds of ore to be roasted.



The standard bed is 100 ft. long by 60 ft. wide, and contains between 4,000 and 5,000 tons. Before the building of the bed is started, about 100 cords of ordinary 4-ft. wood are laid on the ground to a depth of 3 ft. over the full area to be occupied by the bed. By the operation of the ore bridge, coarse ore is now dropped onto the wood until a symmetrical pile of a proper size having the form of a truncated pyramid is built. A covering of fine ore about 1 ft. thick is now spread as uniformly as possible over the whole surface of the pile. This serves to limit the draft and to prevent the roasting proceeding too rapidly. The wood is now lighted and the bed is carefully watched for about a week. Any cracks that develop in the covering of fines must be immediately closed. When all danger from this source is past, the bed is left largely to itself. The roasting may continue for 8 or 10 months, depending mainly on the size of the bed, by which time the sulphur will be reduced to 10 per cent, or somewhat lower. The roasted ore is reclaimed from the beds by a steam shovel having a dipper capacity of  $2\frac{1}{2}$  cu. yd.

**Blast Furnaces.**—The roasted ore is the principal ingredient in the charge to the blast furnaces, but some green ore is always smelted with it, as well as a certain amount of revert. For the grade of matte usually made this mixture is practically self-fluxing. The coke required is about 10.5 per cent of the weight of the charge. The following table gives in condensed form the composition of an average blast-furnace charge and the products of the smelting:

	Tons	Per cent						
		Cu, Ni	Fe	S	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO
Roast ore	5.35	5.50	40.00	10.0	17.50	4.50	2.25	2.50
Green ore	1.85	5.70	43.50	25.0	16.00	5.25	2.50	3.00
Revert...	0.80	5.00	12.00	3.5	26.00	2.75	1.25	1.50
Coke	0.84							
Furnace matte	2.15	23.00	45.50	26.50				
Furnace slag	6.50	0.48	44.00	2.20	31.00	7.50	3.50	2.50
Flue dust	0.21	5.25	35.00	9.00	20.00	4.50	2.40	2.70

One of the larger furnaces now in use smelts about 550 tons of charge per 24 hr. In addition, approximately 100 tons of converter slag are poured into the settler, where it parts with most of its entrained sulphides. The slag from the settlers flows continuously into one-piece steel pots of 225-cu. ft. capacity. The pots are mounted in standard-gage trucks and are taken in trains of eight or ten to the dump, where the still molten slag is poured out. Electric motors turn the pots down for pouring.

Matte is tapped intermittently as required by the converters, and taken to the converter department in sectional cast-iron pots holding about 8 tons. The flue dust that is recovered is sent to the reverberatory plant to be smelted.

Blast furnaces of two sizes are in use, the smaller being 17 and the larger 25½ ft. long. Both are 50 in. wide at the tuyères. The cast-iron hearth plates are supported on 12-in. I-beams. There are four rows of jackets on the sides of the furnaces, the lower two being of cast iron with water pipes embedded, and the upper two of steel with 4½-in. water space. At the dead end of the furnace the lowest jacket is of cast iron, while above it are three steel water jackets. At the front end the lowest jacket is of copper, with a water space similar to the steel jackets. With the brick spout, this copper jacket forms the trap of the furnace. Above the copper jacket,

are three steel jackets similar to those at the dead end. The crucible of the furnace is built of chrome bricks, as is also the spout to the settler.

The settlers have the shape of a distorted oval with a dimension on the longer axis of about 20 ft. They are 5 ft 6 in deep and are lined with chrome brick.

The blast is supplied by Connersville blowers at a pressure in the bustle pipe of 25 oz. From 1,200 to 1,300 cu ft of air per minute is used for each linear foot of furnace. The tuyeres are 6 in. in diameter, spaced about 1-ft centers.

**Reverberatory Plant.**—At the reverberatory plant, most of the fine ore from the mines is further reduced in ball mills until all but about 25 per cent will pass through a 20-mesh screen. Part of the ore received is smelted green without any further crushing. The crushed ore is roasted in seven-hearth Wedge furnaces, 22 ft 6 in in diameter, where the sulphur is reduced from about 25 per cent to between 10 and 11 per cent. The hot calcines are taken directly to the reverberatory furnace and smelted with green ore and flue dust, the whole, with the liquid slag that is also poured in, forming a self-fluxing mixture. The furnace is 112 ft long by 19 ft wide, and is fired with pulverized coal. The weights and analyses of the material charged and of the resulting products are given in the following table.

	Tons	Per cent						
		Cu, Ni	Fe	S	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO
Calcare charged	370	6.50	43.50	10.50	17.00	5.00	2.50	2.75
Green ore charged	80	5.90	12.75	25.80	15.30	4.50	2.25	2.50
Flue dust charged	75	5.20	34.50	9.00	20.50	4.50	2.50	2.50
Total solid charged	525							
Converter slag (liquid)	75	1.50	15.80	2.50	28.00	3.00	1.25	1.50
Total charge	600							
Coal burned	72							
Reverberatory matte produced	200	16.50	51.00	27.00				
Reverberatory slag produced	80	0.47	12.50	1.75	32.00	6.00	3.00	3.00

The slag and matte are handled in the same way as at the blast furnaces.

**Converters.** The converters are of the Peirce-Smith basic-lined type, 37 ft long by 10 ft diameter, and hold a charge of approximately 100 tons. The matte from both the blast furnaces and the reverberatory is charged into the converter, and air from a turboblower, at 12-lb pressure, is blown in. Siliceous flux, which may be either sand, mine rock or quartz, is added to combine with the iron oxide formed and to produce a liquid slag that can easily be skimmed off. After the slag has been taken off, more matte is added and the process repeated until practically all the iron is removed and the converter is full of a high-grade matte, which is the finished product, as far as the smelter is concerned. It contains about 79.5 per cent Cu plus Ni, 20 per cent S, and 0.30 per cent Fe. The finished

matte is poured into molds and, when cold, is broken with sledges to a size convenient for handling and shipped to the refinery in box cars.

To bring the converter to the point where it is full of finished matte requires 50 to 60 hrs., depending on the grade of the matte charged. During that time there will have been charged some 450 tons of combined furnace and reverberatory matte, 160 tons of flux, and perhaps 15 or 20 tons of scrap. The slag skimmed off will amount to about 400 tons, most of which is poured while liquid into the blast-furnace settlers and the reverberatory. The balance, after solidifying, is smelted in the blast furnaces.

**Mond Nickel Co.**—The Mond Nickel Co's. practice differs from that of the International Nickel Co. mainly in that no heap roasting is done, and the fine materials are sintered instead of being treated in a reverberatory furnace. A small experimental oil-flotation concentrating plant is also operated. A somewhat lower-grade furnace matte is produced, and the converter matte is 2 or 3 per cent higher. The equipment also varies somewhat in design, but the treatment throughout is identical in principle.

The concentrating plant is treating a portion of the ore mined that is not considered suitable for direct smelting. Its capacity has recently been increased, and it is now capable of handling about 150 tons of ore per day. The ore treated contains about 25 per cent Cu and Ni. It is crushed in rolls to 4.5 mesh and is then sent without screening or classifying over a Wilfley table, which gives a finished concentrate. The tails from the Wilfley are ground in a ball mill to 100 mesh and the pulp is treated in flotation machines of the Minerals Separation Co. design, producing an additional concentrate and a tails going to waste.

The sintering plant contains four standard 42- by 264-in. Dwight-Lloyd machines, each having a capacity of about 100 tons of sinter per day. The charge to the machines is a mixture of mine fines, concentrates, and flue dust from the smelting operations. The average sulphur in the charge is about 17 per cent, which, in the discharged sinter, is reduced to 7 per cent. The sinter drops into special steel cars in which it is wetted and allowed to cool before being taken to the blast-furnace department.

There are three blast furnaces, each 50 by 240 in., with a capacity of 420 tons of ore per 24 hr. "Each furnace" is carried on structural steel columns, the jackets being hung from I-beams. The crucible rests on three rows of nine supporting columns each 5 ft. in height. It consists of a rectangular steel frame about 6 ft. in width, 21 ft. 9 in. in length, and 25 in. in depth, made of I-beams; the sole plate is of cast iron in four sections. This crucible box is lined with chrome brick around the sides, ends, and bottom, reducing the internal width to 4 ft. 2 in. Above the crucible there is a single tier of water jackets, eight on each side, each 8 ft. 2 in. in height. The width of the furnace is 4 ft. 2 in. at the tuyères; at the top of the water jackets it is 5 ft. 9 in. The settlers are about 15 ft. in diameter. They are placed beside the furnaces and discharge matte and slag from opposite sides.

A typical charge to the blast furnaces would be made up about as follows:

	POUNDS
Green ore	12,500
Sinter	4,500
Scrap	2,500
Total	19,500
Coke	2,000

Limestone is used occasionally. The blast supplied by Connersville blowers is about 25,000 cu. ft. per minute, per furnace, at 32-oz. pressure. The resultant matte contains about 15 per cent Cu and Ni, and goes direct to the basic converters. The slag is disposed of in exactly the same manner as at Copper Cliff. The following table, showing the analyses of the various ores smelted and of the matte and slag produced, is condensed from the *Report of the Ontario Nickel Commission*, which was published in 1917.

	Per cent								
	Cu	Ni	Fe	S	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Insoluble
Levack	0.5	2.8	15.0	23.7	13.5	4.8	2.2	1.3	21.2
Garson	1.9	2.3	29.1	17.2	26.8	9.0	3.4	4.2	35.7
Worthington	3.4	3.0	26.0	17.0	29.0	6.0	3.8	7.0	45.0
Victoria	3.1	1.9	40.2	22.6	17.0	5.1	2.3	1.5	29.3
Sinter	2.7	2.4	30.5	6.9	30.0	7.9	4.4	5.7	45.9
Limestone			5		2.5	0.2	52.6	0.7	2.6
Blast-furnace matte	9.0	11.0	45.0	25.0					
Blast-furnace slag	0.17	0.22	26.6	0.9	31.7	10.1	13.7	5.3	
Bessemer matte	41.0	11.0	0.6	17.0					
Converter slag	0.7	1.3	45.4	1.4	32.1	2.4	1.0	1.1	

At the present time, the analyses may differ somewhat, but, in general, those in the table may be accepted as representative.

The converter department is equipped with three Peirce-Smith basic-lined converters, each 25 ft. long by 10 ft. diameter. They are charged with blast-furnace matte and operated in the same manner as already described. The flux consists largely of siliceous ore from the mine, especially segregated for the purpose. Blast is supplied at 10-lb. pressure, and the volume varies between 5,000 and 7,000 cu. ft. per minute. The finished matte contains about 82 per cent Cu and Ni. After being cast into molds, it is crushed through a jaw crusher to a maximum size of about 1 in. and packed in barrels holding 1,200 lb. for shipment to Wales.

**British-American Nickel Corporation.**—The plant of this company was under construction during the later years of the war, and had been in operation only a short time when it was forced to close down, owing to the post-war slump in the metal market. After over two years' idleness, operations were resumed in June, 1923. In 1924 the property was liquidated at receiver's sale. The following description of the smelter equipment and practice was published by W. A. Carlyle, then managing director of the company, in the *Canadian Mining Journal*, Mar. 18, 1921:

"In the smelter building are two blast furnaces 50 by 360 in. at the tuyères. On a strongly constructed crucible 24 in. high stands the single row of steel water jackets, 14 ft. long, 30 in. wide, inner plate  $\frac{5}{8}$  in., outer  $\frac{3}{8}$  in., with a water space of 5 in. There are two  $4\frac{1}{2}$ -in. tuyères in each jacket, or twenty-four on each side of the furnace, which is tapped at either end, using a water-cooled cast-iron spout for discharging into the settler 20 by 30 by 5 ft., lined with chrome and magnesite bricks. In the converter aisle are two 60-ft. span, 40-ton electric traveling cranes, serving the three Peirce-Smith basic-lined converters 13 by 30 ft. each, with forty-four  $1\frac{1}{2}$ -in. tuyères, electrically rotated. Steel ladles holding 20 tons of matte or 12 tons of converter slag are used.

"This practice has many features different from that followed by the other smelters in the Sudbury district. The ore, averaging 25 per cent  $\text{SiO}_2$ , 35 per cent Fe, 3.7 per cent CaO, 4.3 per cent  $\text{MgO}$ , 6 per cent  $\text{Al}_2\text{O}_3$ , and 19 per cent S, is smelted without any preliminary roasting, and the only flux used is converter slag, containing 16 per cent  $\text{SiO}_2$ , 52 per cent Fe, 3.5 per cent CaO and 3.5 per cent  $\text{Al}_2\text{O}_3$ , the charge consisting of 70 to 75 per cent ore, the balance flux with 10.5 per cent coke on the charge. The resulting slags contain 35.5 per cent  $\text{SiO}_2$ , 30 per cent Fe, 5.5 per cent CaO, 13 per cent  $\text{Al}_2\text{O}_3$ , and 0.24 to 0.34 per cent Ni plus Cu plus Co.

"The low-grade matte from this furnace, containing 11 to 13 per cent Ni plus Cu, is poured into the converters, and blown up to the usual matte, containing 80 to 82 per cent Cu, Ni, and a trace of Fe, which is transferred to an oil-fired furnace, and in running from thence through a strong stream of water is successfully granulated, then wheeled into box cars and shipped to the refinery.

"In the converter method, the flux mainly used is ore fines with some siliceous gravel or sand. One aim is to keep the silica in the converter slag as low as possible, often averaging for days under 13 per cent. This slag is poured in part into large 20-ton cars, poured outside the building onto shallow beds lined with ore fines, broken and lifted by locomotive cranes using clam-shell buckets and sent to the smelter bins. Part of the slag is poured into the settlers."

The capacity of the furnaces is shown by the following figures, which were published in the *Engineering and Mining Journal*, Aug 13, 1921. The amounts given are the tonnages smelted per 24 hr., in one 30-ft. furnace, over a period of a week:

	Tons ore	Tons flux	Tons coke
First day	811 20	327 60	119 00
Second day	811 20	326 60	116 60
Third day	764 90	293 60	107 30
Fourth day	712 85	269 00	99 85
Fifth day.	713 60	306 70	116 70
Sixth day	896 40	315 40	125 40
Seventh day	899 10	316 35	127 45
Total	5,609 25	2,156 25	812 30
Average per day	801 32	308 03	116 04

The large amount of converter slag produced by bessemerizing a matte of such low grade as 10 or 12 per cent has proved troublesome to cope with, and it seems probable that it will be found advisable to roast a certain portion of the ore in order to raise the grade of the furnace matte.

The method of smelting the Norwegian ores is closely similar to that practiced in the Sudbury district, but is on a much smaller scale.

**Matte Refining.**—There are two principal methods used commercially today for the refining of the copper-nickel matte resulting from smelting operations in Canadian (Sudbury) ores—that used by the International Nickel Co. (sometimes called the Orford process, from the name of this company's former Orford works); and the Mond process. The refining of nickel-iron matte from New Caledonia ores has already been described above.

**The International Nickel Co. Process.**—This process is based upon the fact that, in a molten system containing nickel sulphide, copper sulphide, and sodium sulphide, in general, two liquid layers are formed, the upper carrying the bulk of the sodium and copper sulphides and the lower the bulk of the nickel sulphide. A separation is made of these two layers.

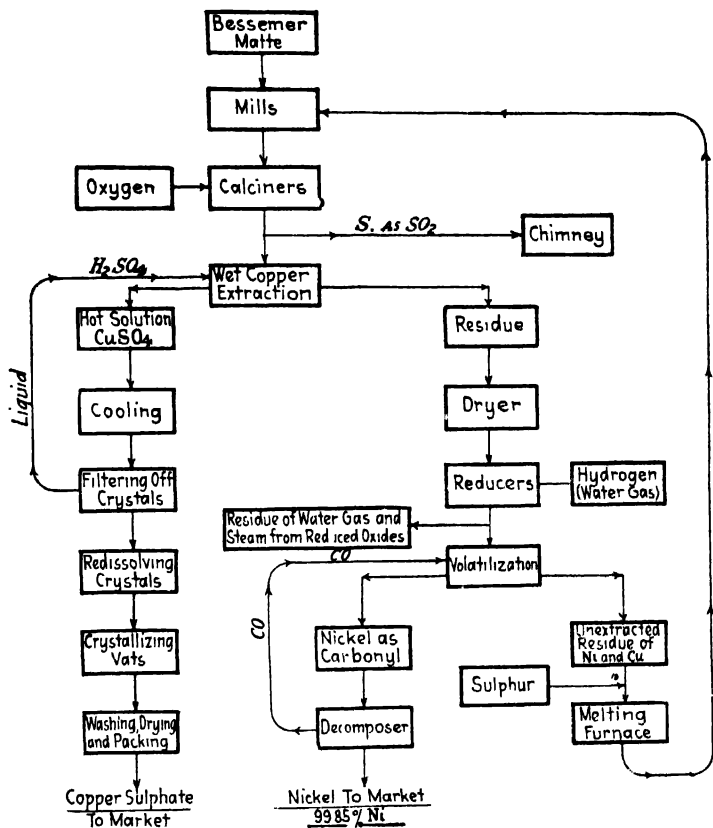


FIG. 2.—Mond-process flow sheet.

The bessemer matte, containing approximately 54 per cent Ni, 26 per cent Cu, 20 per cent S, and 0.30 per cent Fe, is shipped from Copper Cliff to Port Colborne, Ont., the location of the company's new refinery. This, one of the most recently constructed nickel refineries in the world, was blown in at the end of 1918. As it has been thoroughly described in the technical press, no details will be given here.

The bessemer matte is charged into a standard water-jacketed blast furnace with coke and revert top soda flux from a subsequent operation. The essential reagent is sodium sulphide or sodium sulphate, the latter being reduced by the coke of the charge to the former. On solidification of this first smelting in pots a top and bottom formed effecting the dividing line between the two metals. About 90 per cent of the total copper in the form of top is transferred to Peirce-Smith converters, where it is blown to blister copper, ready for the market. The separation between top and bottom is marked by a clean line of cleavage.

The bottom, containing the nickel, goes to a second smelting with soda flux. From the second smelting the top goes back to the first smelting of bessemer matte.

This second bottom—nickel sulphide—shows the following analysis: Ni, 70 per cent; Cu, 0.90 per cent; Fe, 0.25 per cent. From a ball mill the nickel sulphide goes to leaching tanks, where the mechanically contained soda is washed out with water and the iron with dilute sulphuric acid. The nickel sulphide is then given one chloridizing roast and leached to remove the copper, and a second roast with soda ash to remove all fractional remaining impurities. The resulting black oxide of nickel, of the following analysis—Ni, 77.60; Cu, 0.10; Fe, 0.25; Si, 0.10; and S, 0.015 per cent—is ready for the market or reduction to metal in the open-hearth furnace. It is tapped from the furnace into pig nickel, nickel shot, and nickel anodes (for analyses see Table 1, p. 1309; for flow sheet see p. 1297).

The nickel anodes go to the electrolytic refinery. Tank sludge from this process is treated for the recovery of precious metals of the platinum group.

**The Mond Process.**<sup>1</sup>—Bessemer matte, assaying approximately 40 per cent Ni, 40 per cent Cu, and 15 to 17 per cent S, and small amounts of iron, is produced at the company's smelter, at Coniston, Ont., crushed to 1½-in. size and shipped in barrels to the refinery at Clydach, South Wales.

The crushed matte is ground in ball mills to pass a 60-mesh screen, and roasted to oxides in long mechanical calcining furnaces. This oxide is then leached with sulphuric acid, to remove a large part of the copper as copper sulphate. This hot copper sulphate solution, carrying the undissolved nickel oxide and some copper in suspension, is passed over rotating vacuum filters to separate the solid matter from the solution, which is then passed through a series of lead-lined cooling vessels, causing the copper sulphate to drop out in solid form, which is separated from the liquid by vacuum filters similar to those used for obtaining the nickel residues.

The crude copper sulphate is redissolved and the concentrated solution run into large vats and allowed to crystallize. The blue-vitriol crystals are washed with water to remove acid, dried, and packed in casks for the market.

**Nickel Extraction.**—The nickel oxide residue, free from most of the copper, is dried and fed into vertical cylinders, divided into a series of sections by horizontal plates. A vertical shaft, equipped with radiating arms or stirrers, passes through these horizontal plates and discharges the material from each section to the next lower. The cylinder is heated to about 300°C. and hydrogen (water gas) is pumped through the descending nickel oxide, reducing it to the metallic state. The reduced material is cooled and passed into another cylinder, called a volatilizer, similar to the reducer, except that it is not heated. As the reduced material passes down through the cylinder, it meets a stream of carbon monoxide gas, which combines with the nickel, forming nickel carbonyl ( $\text{Ni}(\text{CO})_4$ ). This reaction takes place at ordinary room temperature.

The gas stream from the volatilizer, now carrying nickel carbonyl, is forced through another vertical cylinder called a decomposer. This cylinder is filled with nickel pellets, which are constantly being drawn off at the bottom and recharged at the top. The decomposer is heated to about 150°C. (270°F.), at which temperature the nickel carbonyl breaks down, depositing its nickel on the pellets. The carbon monoxide gas is returned to the volatilizer. The friction caused by the continual motion of the pellets detaches minute particles, which grow larger from the nickel deposited on them. The pellets drawn from the bottom pass over a screen and the smaller sizes are recharged at the top. The oversize are produced for the market. This product will contain Ni, 99.80 per cent; S, trace; Fe, 0.06 per cent; C, 0.09 per cent; Si, trace; Cu, none.

<sup>1</sup> Taken largely from "The Metal Industry," Feb. 17, 1922, and the Report of the Royal Ontario Nickel Commission.

The residue from the volatilizer, consisting of copper and nickel, is melted with sulphur to a copper-nickel matte and reverts to the initial step in the process, i.e., similar to the bessemer matte.

**The Hybinette Process.**—This process was employed by the British-American Nickel Corporation, at its refinery at Deschenes, Que. Bessemer matte of the following composition—Ni, 53, Cu, 28, S, 18, and Fe, 0.25 per cent—was produced at the company's smelter at Nickelton, Ont. The matte was granulated and shipped to the refinery. The granulated matte was screened through 10 mesh and charged into cementation tanks, through which flowed the foul electrolyte from nickel-plating tanks. Bessemer matte was semimetallic, and the metallic portion cemented the copper, an equivalent amount of nickel went into solution. To facilitate this metal transfer, each tank was equipped with hard-lead steam coils (about 70°F is necessary). The copper-free electrolyte and the foul solution from plating tanks flowed in opposite directions through a heat interchanger in which a part of the heat in the purified liquor was transferred to the foul liquor before entering the cementation tanks.

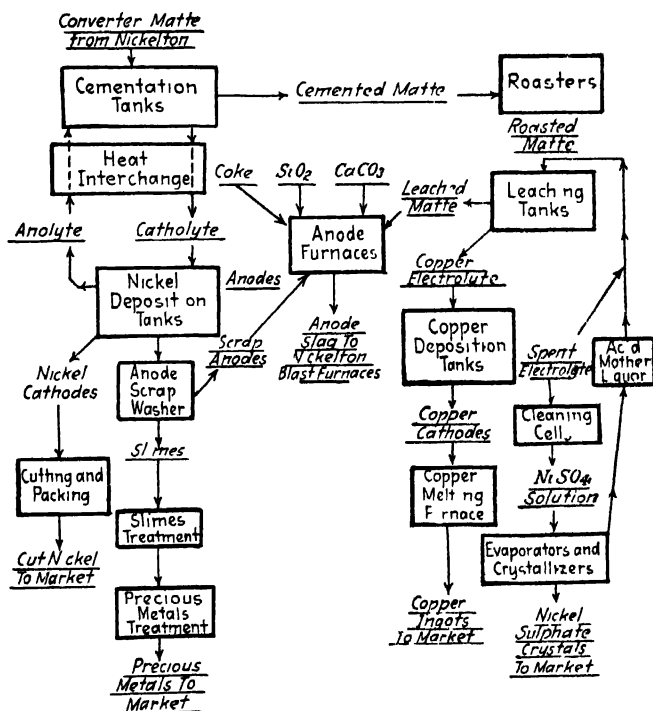


FIG. 3.—British-American Nickel Co. flow sheet

The spent matte from the cementation tanks, then containing about 44 per cent Cu and 38 per cent Ni, was excavated and sent to eight-hearth Wedge roasters, and roasted to about 1 per cent S. The hot cakes passed over a screen, the oversize was crushed and returned to roasters, and the fines were discharged into a launder, through which leaching solution conveyed them to leaching tanks of about 90-ton capacity. This leaching solution was depleted electrolyte from the copper-plating tanks (30 g per liter of Cu and 80 g per liter of  $H_2SO_4$ ).



The copper-enriched solution from leaching tanks (Cu, 50 g. per liter; and  $\text{H}_2\text{SO}_4$ , 50 g.) passed through clarifying cones and thence to a series of three-tank, cascade electrolytic deposition tanks. These tanks were lead lined and contained eight cathodes and nine lead anodes. The overflow from the third tank of the series returned to roaster launders as leach liquor.

As a certain amount of nickel was dissolved with the copper and accumulated in the copper leach liquor or electrolyte, a portion of the spent electrolyte was continuously removed and passed through a separate series of plating tanks, where the copper was practically all removed. This copper-free solution was evaporated and the nickel crystallized as single nickel salts ( $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ ). Mother liquor, rich in acid, was returned to leaching tanks.

The nickel electrolyte was also continually enriched with nickel in the cementation tanks, where the copper cemented on the matte was replaced by an equivalent amount of nickel. It was necessary, therefore, to withdraw continually portions of the solution which was evaporated and crystallized as above. The leached, roasted matte was excavated, mixed with coke breeze and limestone, and melted in a three-phase resistance furnace. The metal was tapped intermittently into a brick-lined ladle, and poured into cast-iron anode molds (24 by 36 in.). Anodes contained about 68 per cent Ni, 26 per cent Cu, and 0.40 per cent Fe.

The anodes were encased in bags to catch slimes and suspended in lead-lined tanks (36 anodes and 35 cathodes). Cathodes consisted of iron or copper plates (24 by 36 in.) suspended in "Hybinette bags," consisting of wooden frames with canvas sides, acting as diaphragms.

Copper-free nickel electrolyte from cementation tanks (previously described) was fed to cathode bags through rubber tubes from a lead header at a rate sufficient to maintain a head of about 1 in. over the level in the anode compartment. This was to prevent anolyte containing copper from flowing into the cathode bags and contaminating the nickel. The iron or copper cathodes were painted with graphite to facilitate stripping. Nickel sheets weighing about 30 lb. were stripped from cathodes about every 10 days, washed with dilute sulphuric acid, and cut into small squares for shipment. Or they were melted in electric furnace and cast into ingots.

Electrolytic nickel analyzed about: Ni, 98.25; Co, 0.75; Cu, 0.03; Fe, 0.50; C, 0.10; and Pb, 0.20 per cent.

Anode scrap was remelted and cast into molds. Slag from the melting furnace was shipped back to the smelter for retreatment. Slimes from the anode tanks were treated for the recovery of precious metals.

**Rolling-mill Operations.**—A portion of the refined nickel produced is manufactured into malleable nickel in the usual commercial forms: rods, sheets, forgings, tubes, etc. In addition, the International Nickel Co. produces its alloy, Monel metal, in these forms.

The rolling mill operations by which these forms are produced resemble somewhat those used in the manufacture of steel, and the equipment used is not very different from standard steel-mill equipment. The operations of the International Nickel Co., at its new mill in Huntington, W. Va., represent the most modern practice in this respect and will serve as a typical illustration of such operations.

**Products.**—This plant produces commercially pure malleable nickel, Monel metal, and copper-nickel alloys (constantan). The nickel is produced by remelting pig nickel from its Port Colborne refinery, and the copper-nickel alloys by remelting pig nickel and ingot copper. The Monel metal is produced, however, direct from bessemer matte by roasting in mechanical furnaces, followed by reduction and refining of the copper-nickel oxide in open-hearth or electric furnaces.

In the production of all of these metals the molten metal, after melting and refining, is poured into chilled ingots, which are overhauled, hammer cogged to blooms, then hot rolled to rods or sheets

The process followed in casting ingots has been developed by years of careful practice and attention. The standard size of ingot is 14 by 14 by 60 in. and weighs about 2 tons as cast. These ingots are poured at a temperature of about 2900°F, after being deoxidized in the ladle by metallic magnesium. The molds are iron with preheated sand-lined tops. The ingots, after cooling, are stripped from the molds, marked with heat numbers, and taken to a Newton saw, where the head is sawed off. The head amounts to roughly 23 per cent of the gross weight. Next, the ingot is skinned on a specially designed milling machine, which takes a 1/4-in. deep cut over each face. After milling, the ingot is inspected for any imperfection and —if necessary—chipped in spots with a pneumatic chisel. After chipping, the ingot is heated for forging in neutral atmosphere to about 2000°F in a carefully controlled gas-fired furnace with surface-combustion burners and forged under an 8-ton steam hammer to blooms 8 by 8 in. for rods and bars and 9 by 5 in. for sheet bars, each bloom weighing about 1,000 lb. The blooms are overhauled with chipping hammers, then heated and rolled on a 24-in. bar mill into sheet bars for sheet rolling or into billets for the merchant mill. Sheet bars are rolled to 8 in. and 12 in. wide and any thickness required, and cut to length.

**Sheet Mill.**—The sheet bars are pickled and overhauled, then heated in a gas-fired furnace in neutral atmosphere to about 2000°F, and hot rolled on a 30-in. diameter hot mill according to steel-mill practice. These mills will handle sheets up to 50 in. wide and will produce gages from 0.015 to 0.250 in. lengths from 8 ft. up to 12 ft., depending upon width and gage. After hot rolling, the sheets are rough squared, pickled, and annealed in sealed boxes with powdered charcoal at 1600°F. After the first anneal, the sheet is leveled, either by a stretcher or a roller leveling device, cold rolled two passes for size, and reannealed, resquared, inspected, stenciled with size and gage, and sent to the warehouse for shipment. A most careful control of the heating conditions is maintained throughout this practice as an essential to best-quality product.

Cold rolled sheets are produced from the hot mill product following standard steel practices, also employing special modern type of Cluster Mill capable of effecting cold reductions from 25 to 40 per cent without further annealing operations. Sheets of this character are produced to maximum width of 36" and in the usual standard gauges. These products have a natural high lustre which is further developed to high polish on modern automatic polishing machines capable of accommodating standard size sheets.

**Merchant Rolls.**—Billets for rolling into rods and bars on the merchant mills are inspected for seams, pipes, cheeks, etc. and chipped free of defects.

The overhauled billets are heated to 2000°F for rolling in gas-fired heating furnaces of reverberatory type with surface-combustion burners. These furnaces are under pyrometer control and Orsat gas readings are taken periodically to maintain proper furnace atmosphere, which should be nearly neutral.

Billets are rolled into rods on four different mills according to size of rod required. Rods from 2- up to 4-in. diameter and equivalent sections are rolled on a 20-in. diameter mill of the hand round type. The mill is extra-heavy construction, motor driven. The billets are rolled according to steel practice, except that reductions per pass are worked out especially for nickel products.

After rolling, which is done in one heat, the resulting bars, in commercial lengths of 8 to 20 ft., are cropped by hot sawing and are rough straightened on a cooling bed.

When cold, the bars are gaged, inspected for any defects, and sent to the warehouse for shipment.

Wire rods and small coiled flats are rolled on a 9-in. wire mill. This mill has several interesting features. The layout consists of two separate mills in line with each other of 9-in. pitch diameter, one being a five-stand roughing mill, the other a four-stand finishing mill. Added to these is a 14-in. Belgian roughing mill. This equipment allows coils of approximately 100-lb. weight to be finished in one heat in rod diameters of  $\frac{1}{16}$  down to  $\frac{3}{32}$  in. Power reels take the finished wire rod from the finishing pass and coil it to suitable size for handling in shipment and in subsequent working by the wire manufacturer. The finished material undergoes inspection and is finally sent to the warehouse for shipment.

The rolling of nickel and Monel metal not carried out at quite such high speed as is sometimes practiced with steel. The capacity of the finishing mills mentioned is about 100 tons per day. More attention is given to the quality of the finished produce than to establishing production records.

**Cold-drawn Rods.**—A cold-drawing department has been added to the original mill installed. This consists at present of two straight draw benches of 25 tons capacity. Each bench will handle rods up to 3-in. diameter or equivalent cross-section in lengths up to 20 ft. Rods are carefully selected from hot-rolled stock, pickled, and drawn one pass with  $\frac{1}{16}$ -in. reduction. The rods are then annealed and given a second pass with approximately the same reduction to finished size. Finished rods are inspected and straightened in a Medart machine and are then ready for shipment.

**Seamless Nickel Tubing.**—Standard hot finished seamless nickel tubing is regularly produced by steel methods in the plant of one of the larger tube manufacturers. These products are later reduced to cold drawn tubing in the equipment of the International Nickel Company at Huntington, W. Va., in a manner similar to the production of cold drawn rods. The sizes range from 1 to 4 inches in diameter and are of standard mill lengths.

**Reduced Nickel.**—A special product produced at the Huntington plant of the International Nickel Co. is so-called reduced nickel. Reduced nickel is metallic nickel in a finely granular form, produced by reducing the black oxide of nickel with charcoal at a temperature slightly below 1500°F. It is dull gray, and magnetic.

It is of use where a highly soluble form of nickel is desired and where the granular form is acceptable. One of its large uses is in the manufacture of nickel salts. A typical analysis of INCO reduced nickel is as follows: Cu, 0.26; Ni, 97.80; and soluble Ni, 95.80 per cent.

The wet oxide to be reduced is mixed by piling and turning with about 30 per cent of its weight of ground charcoal. The intimate mixture is then charged into an oil-fired roasting furnace with flat rectangular hearth and working doors on each side, which allow hand rabbling of the charge during the reducing process.

The charge in the furnace is leveled off to a depth of about 4 in. The oil burner is then lighted and heat is gradually applied to the charge. It is rabbled every 30 min. to insure even heating and to work the charge toward the front end of the furnace. Additional charcoal is added before the final rabble, or after about  $3\frac{1}{2}$  hr., and then the charge is drawn into iron drums, covered with charcoal and sealed.

The drum is allowed to cool for at least 24 hr. The seal is then broken, the material dumped on the floor, screened through  $\frac{1}{4}$ -in. mesh wire screen, and put through mag-

netic separators to clean it from charcoal. The separated reduced nickel ready for shipment is rather finely granular. A screen test shows that on an average

90 per cent passes	10 mesh
80 per cent passes	20 mesh
50 per cent passes	50 mesh
20 per cent passes	100 mesh
10 per cent passes	150 mesh

This product is put up in barrels, weighing about 1,000 lb. each, and is then ready for shipment.

**Properties and Commercial Applications.**—Nickel is a silvery-white metal having a strong luster. It is malleable, ductile, somewhat magnetic, harder and stronger than iron, resistant to abrasion, and of high melting point. It is very highly resistant to the action of air, water, non-oxidizing acids, fused alkalis and salts, either fused or in aqueous solution. It is also remarkably resistant to oxidation at high temperatures. It has a magnetic transformation point occurring at about 320°C. in commercial grades.

While nickel is primarily divalent, a few relatively unstable compounds are known in which it is trivalent. A peroxide ( $\text{NiO}_2$ ) is also known. Nickel is, with cobalt and iron, a member of the eighth group of the periodic system. Its atomic weight is 58.68. In normal solutions of its salts, nickel has a solution pressure of about 0.6 volt against the calomel electrode. Its electrochemical equivalent is 0.30425 mg. per coulomb.

Nickel and its compounds exhibit strong catalytic activity in all types of reactions, as illustrated in its commercial use for the hydrogenation of oils.

Metallic nickel gives to its alloys strength, ductility, and resistance to corrosion. With such metals as copper and gold it acts as a powerful decolorizing agent.

**Distribution of Nickel.**—Nickel is widely used industrially. Arranged roughly in order of their relative importance from the tonnage standpoint, the paths of distribution for nickel are as nickel steel, Monel metal, nickel-silver and copper-nickel alloys, electroplating, nickel-chromium-iron "heat resisting" alloys, malleable nickel, coinage, nickel salts for catalysts, etc., and nickel oxide for use in the ceramic industry.

TABLE 1. COMMERCIAL NON-MALLEABLE GRADES OF NICKEL

Grade	Form	Analysis, per cent						Uses
		Ni-Co	Cu	C	Fe	Su	S	
Electrolytic <sup>1</sup>	24" X 36" - 100 lb plates	99.80	0.04	Tr	15	Nil	Tr	Highest-grade malleable alloys
Shot "X"	Granulated in water	99.15	0.18	12	38	10	0.025	Non-ferrous alloys and crucible nickel steel
"XX"	Granulated in water	99.45	0.08	10	25	05	0.008	
"A"	Granulated in water	98.75	0.18	45	38	22	0.025	Platers' anodes
"F"	Granulated in water	91.75	0.20	30	1.85	5.75	0.025	
Ingot or pig	25-50 lb pig	99.20	0.30	03	45	03	0.035	Open-hearth or electric furnace steel
Reduced nickel oxide	Powder	98.75	0.15		50			Nickel salts

<sup>1</sup> Electrolytic nickel is malleable, but is seldom used for this property.

Nickel is marketed in various forms, depending on the use to which it is to be put. These are: (1) grains, cubes, rondelles, or powder, reduced from the oxide at low temperature without being fused; (2) nickel shot, nickel deposited in concentric layers from nickel carbonyl (gas) without being fused; (3) electrolytic cathode sheets; (4) blocks or shot obtained by reducing nickel oxide at temperatures above the melting point of nickel and casting the resulting metal or pouring it into water, without deoxidation; (5) malleable nickel, produced in the same manner as (4), except that it is treated with a deoxidizer before pouring; (6) nickel salts; (7) nickel oxide.

Most of the commercial production of nickel falls in class (4).

One of the larger producers makes nickel in the grades listed in Table 1.

**Malleable Nickel.**—The properties of malleable nickel at ordinary temperatures are given in Tables 2 and 3 and at elevated temperatures in Table 4.

TABLE 2.—PHYSICAL PROPERTIES OF MALLEABLE (99 PER CENT) NICKEL

(Commercially pure nickel)

Density (specific gravity), 8.84.

Weight per cubic inch, 0.319 lb.

Melting point, 1450°C. (2640°F.).

Shrinkage (pattern),  $\frac{1}{4}$  in. per foot.

Linear coefficient of thermal expansion:

25 to 100°C., 0.0000130 per degree.

25 to 300°C., 0.0000145 per degree.

25 to 600°C., 0.0000155 per degree.

Electrical resistivity, 64 ohms per mil foot (10.6 microm-cm).

Conductivity about 16 per cent of that of copper.

Coefficient of electrical resistivity, 0.0041 per degree Centigrade, or 0.0023 per degree Fahrenheit.

Optical reflection coefficient, 65 per cent.

Thermal conductivity, 0.14 c.g.s. units (about 17 per cent that of copper).

Specific heat (20 to 1400°C.), 0.130 cal. per gram

Latent heat of fusion, 73 cal. per gram.

Magnetic induction at 100 gaussess field strength, 5,000 gaussess.

Young's modulus of elasticity, 30,000,000 lb. per square inch.

Torsional modulus, 10,000,000 lb. per square inch.

Poisson's ratio, 0.33.

TABLE 3 —MECHANICAL PROPERTIES OF 99 PER CENT NICKEL

Form of material	Tensile properties				Hardness		
	Yield point, pounds per square inch	Tensile strength, pounds per square inch	Elong- ation in 2 in., per cent	Reduction of area, per cent	Brinell		Sclero- scope
					500 kg	3 000 kg	
Rods, hot rolled	20 000-30,000	70,000-80,000	40-50	50-70	90-110	110-130	15-18
Sheet							
Annealed	15,000-25,000	60 000-75,000	35-45		80-100		12-14
Cold rolled, hard	85,000-105,000	90,000-110,000	1-2		130-160		30-40
Wire							
Annealed	15 000-25 000	60 000-75,000	20-30				
Hard drawn	110,000-130,000	120 000-140 000	1-2				
Castings	20 000-30,000	50,000-60,000	20-30		80-100		12-15

Nickel and some of its alloys retain their physical properties to a relatively high degree at elevated temperatures. The data of Table 4 were obtained by the International Nickel Co.

TABLE 4.—PROPERTIES OF 99 PER CENT MALLEABLE NICKEL AND OF SOME OF ITS ALLOYS AT ELEVATED TEMPERATURES

Temperature, degrees Fahrenheit	Rolled "A" nickel	Rolled Monel metal	20 per cent Cupro nickel	Temperature, degrees Fahren- heit	Rolled "A" nickel	Rolled Monel metal	20 per cent Cupro nickel
Tensile strength, 1,000 lb. per square inch				Yield point, 1,000 lb. per square inch			
70	81	90	63	70	24	45	
200	82	86	61	200	24	38	
400	84	84	58	400	24	34	
600	83	82	51	600	23	32	
800	83	78	41	800	21	30	
1000	58	60	30	1000	19	28	
1200	45	45	18	1200	17	24	
1400	30	22	6	1400	13	15	
1600	17	15					
1800	11	8					
2000	8	5					
Elongation, per cent in 2 in.				Reduction of area, per cent			
70	51	46	28	70	70	69	
200	51	45	27	200	68	68	
400	52	44	26	400	68	66	
600	51	42	24	600	68	64	
800	50	38	22	800	66	62	
1000	50	29	17	1000	75	31	
1200	48	13	14	1200	76	15	
1400	50	8	23	1400	78	10	
1600	33	14	27	1600	32	15	
1800	36	18		1800	40	25	
2000	70	22		2000	99	29	

Malleable nickel is the only grade in the production of which deoxidizers are used. Deoxidation is accomplished by the addition of manganese and magnesium in the crucible or ladle before pouring into ingots or castings. The carbon content is adjusted to 0.10 to 0.30 per cent by adding charcoal or nickel oxide and the metal raised to pouring temperature (2800 to 3000° F). If an electric furnace be used, the deoxidizers should be added in the furnace if possible. Manganese is added first, either as such or as ferromanganese, to the extent of 0.25 to 2.0 per cent. Magnesium is added to the extent of 1.5 oz. per 100 lb. of nickel. It must be held in tongs and plunged below the surface of the molten metal and an excess must be avoided.

The commercial forms of malleable nickel are: hot-rolled and cold-rolled sheets; hot-rolled and cold-drawn rods; cold-rolled strip; seamless and welded tubing; pipe;

wire; forgings; castings; and fabricated forms, such as screen, filter, and wire cloth, wool, etc. The metal may be machined, welded, forged, or brazed.

At least twelve countries use nickel for subsidiary coinage and it is largely used for household and ornamental stampings and fittings.

For its resistance to corrosion it is used extensively for cooking utensils, dairy and food-handling machinery, laboratory apparatus and equipment for operations, digestions, evaporation, and transport in the manufacture of dyes and intermediates, essential oils, etc. Kettles, stills, fusion pots, especially for cyanide fusions, and other apparatus are made of malleable nickel, castings of which are quite general for heavy equipment of this type. Some nickel is used for valve trim.

For its resistance to oxidation at high temperatures, nickel is used as heat-resisting castings, parts of glass-making machinery, lehrs and annealing furnaces, burner parts, as wire for spark-plug electrodes, suspension wires of electric-light bulbs, resistance pyrometer tubes, and for combustion boats used in the reduction of tungsten and molybdenum oxides. Nickel wire with high manganese content is practically standard for spark-plug electrodes. The "D" nickel of the International Nickel Co. contains from 3 to 6 per cent of manganese. It has a specific resistivity of 20 microhms per centimeter cube and a temperature coefficient of 0.0020 per degree Centigrade.

Rabble shoes of cast nickel, exposed in Edwards-type roasting furnaces to sulphurizing and oxidizing gases at 600 to 1000°C. and to severe abrasion, outlast cast-iron shoes about four and a half times.

**Electroplating.**—In the aggregate rather substantial quantities of nickel are consumed in such operations, the major portion of which is consumed in the form of platers' anodes which vary in nickel content from 85 to 99 per cent. The chief impurities contained are iron and carbon which in some cases is added especially to promote rate of corrosion. The modern tendency, however, in these operations is towards the higher purity product. Nickel plating is used for improving in appearance and protecting from corrosion the base metal to which it is applied. Deposits can be effected satisfactorily on iron, brass, copper, zinc and many of the common alloys.

Relatively only a small amount of nickel is used in non-metallic combinations. The sulphate and the double-ammonium sulphate are used in nickel plating, while the carbonate, nitrate, and formate are used as sources of reduced nickel for catalysts in chemical processes. The oxide is used sometimes for the under, or holding, coat in enameling steel and for coloring glazes in pottery manufacture. The hydroxide is used in the Edison alkaline storage cell, where it is reversibly altered to nickelic hydroxide during charging and discharging.

**Nickel-copper Alloys.**—Nickel and copper are mutually soluble in all proportions, giving solid-solution alloys which are malleable both hot and cold. The malleability is obtained by the use of deoxidizers in the same manner as for nickel. Alloys low in nickel have a characteristic pinkish color, which fades progressively until at 25 per cent or more nickel the color is similar to that of pure nickel.

The alloys used commercially range from 2.5 to about 70 per cent of nickel. For special properties, characteristic of the alloys of different nickel content, they are used for driving bands for shells, bullet jackets, condenser tubes, resistance to corrosion and erosion, turbine blading, coinage, valve seats and parts, resistance and pyrom-

eter wire, and remelting purposes. Most of the alloys are known by special names in the industry. More complete information is given in the references cited in the Bibliography at the end of this section.

**Monel Metal.**—Monel metal is the trade-marked name of a nickel-copper alloy which contains approximately 67 per cent Ni, 28 per cent Cu, and 5 per cent of constituents of lesser importance, chiefly iron and manganese. It is a natural alloy, there being no separation of the two major constituents nor alteration of their relative proportions in the process of reduction from the ore in which both occur. This alloy resembles nickel in color, finish, and properties. It combines, in a single alloy, high mechanical properties with resistance to corrosion, oxidation, and erosion. Its mechanical properties are retained to a large extent at elevated temperatures, as may be seen in Table 4.

This metal may be rolled, drawn, cast, forged, machined, welded, and soldered. It may be had in the form of pig, shot, hot-rolled and cold-rolled sheets, hot-rolled and cold-drawn rods, bars, strip, wire, welded tubing, castings, forgings and fabricated forms, such as wire screen and cloth, filter cloth, bolts and nuts, nails, tacks, rivets, cable, chain, balls, etc.

The properties of Monel metal are given in Tables 5 and 6.

TABLE 5.—PHYSICAL PROPERTIES OF MONEL METAL.

Density (specific gravity), 8.80.

Weight per cubic inch, 0.318 lb.

Melting point, 1300 to 1350°C. (2370 to 2460°F.).

Shrinkage (pattern),  $\frac{1}{4}$  in. per foot.

Linear coefficient of thermal expansion:

25 to 100°C., 0.000014 per degree.

25 to 300°C., 0.000015 per degree.

25 to 600°C., 0.000016 per degree.

Electrical resistivity, 256 ohms per mil. foot (42.5 microhm-cm.).

Conductivity about 4 per cent of that of copper

Coefficient of electrical resistivity, 0.0019 per degree Centigrade, or 0.0011 per degree Fahrenheit

Optical reflection coefficient, 60 per cent

Thermal conductivity, 0.06 c.g.s. units (about 7 per cent of that of copper).

Specific heat (20 to 1300°C.), 0.127 cal. per gram.

Latent heat of fusion, 68 cal. per gram.

Magnetic induction at 100 gaussess field strength:

Cast metal, 500 gaussess.

Rolled metal, 1,000 to 1,500 gaussess.

Magnetic transformation point, 93 to 95°C.

Young's modulus of elasticity, 25,000,000 lb. per square inch.

Torsional modulus, 9,500,000 lb. per square inch.

Compression tests on hot-rolled rods showed: proportional limit, 35,000 to 40,000 lb. per square inch; yield point, 60,000 to 70,000 lb. per square inch. Resistance to alternating stress in rotating-beam machines, approximately 100,000,000 alternations at proportional limit, *i.e.*, the endurance safe limit. Izod test, 100 ft. lb. on standard specimen. Charpy test (standard test piece), hot-rolled rod, 100 to 200 ft. lb. to rupture.



TABLE 6 — MECHANICAL PROPERTIES OF MONEL METAL

Material	Tensile properties				Brinell hardness		Torsional properties			
	Proportional limit, pounds per square inch	Yield point, pounds per square inch	Tensile strength, pounds per square inch	Elongation in 2 in. per cent	3 000 kg	500 kg	Proportional limit, pounds per square inch	Yield point, pounds per square inch	Ultimate strength, pounds per square inch	Shearing deformation, inches per inch gage length
Hot-rolled rods and rounds up to 1 in. diameter	39 700*	51 300	91 500	4½	144	113	25 200	30 000	62 000	2 78*
1½- to 1½-in. diameter	47 700*	59 600	93 200	37	162	130	29 700	38 600	61 800	2 93
1¾- to 2½-in. diameter	40 200*	51 900	90 300	42	161	127 f				
2½- to 3½-in. diameter	52 200	41 900	88 900	46	147	120	20 200	26 700	63 300	2 64
Over 3½-in. diameter	37 200*	50 300	88 400	43	152	120	24 200	32 200	62 100	2 57
Hexagons	49 100	60 600	92 300	38	167	133				
Rectangles	33 800	47 000	89 800	47	144	114				
Cold drawn rods		75 000	100 000	20	200					
		80 000	110 000	30	210					
Castings		30 000	65 000	25	105					
		40 000	80 000	35	115					
Sheet										
Annealed		25 000	65 000	35		100				
		35 000	75 000	45		120				
Cold-rolled		90 000	100 000	1		180				
		110 000	120 000	2		200				
Wire										
Annealed		25 000	65 000	20						
		35 000	75 000	30						
Drawn		100 000	110 000	1						
		130 000	140 000	2						

\* Tensile properties and hardness average, except where ranges of values are indicated, torsional values average of 72 tests

**Chemical Properties and Uses.**—Monel metal is widely used for its resistance to corrosive conditions. It is used against anhydrous ammonia, either liquid or gaseous; ammonium hydroxide solutions; solutions of or fused caustic alkalis and carbonates; fatty and other organic acids; seawater; solutions of neutral salts; gasoline and mineral oils; phenol and cresols; photographic chemicals, except solutions containing silver, urine, dry mercury, dyeing, and bleaching solutions; alcoholic and other beverages. It is also highly resistant to sulphuric, dilute phosphoric, hydrocyanic, hydrofluoric, acetic, and citric acids, fused cyanides, ferrous sulphate, and dry chlorine. The metal is attacked by solutions which are strongly oxidizing or contain easily reducible compounds and by molten lead and zinc. It is not resistant to hydrochloric, nitric, nitrous, sulphurous, chromic, or concentrated phosphoric acids or to solutions of ferric salts.

It is used for marine propellers, deck hardware, and parts of ships exposed to the action of sea water; pumps, pump liners, rods and valves for sea water, mine waters, and corrosive solutions generally; mining machinery; mine screens; machinery and equipment for dyeing and bleaching; miscellaneous parts of apparatus exposed to corrosive conditions in the chemical and oil industries generally; screen cloth, filter cloth, roofing, etc. Monel-metal pins and rods in sulphuric acid pickling tanks in the steel industry have exceptionally long life. Large quantities of metal were used in roofing the trainsheds of the Pennsylvania Terminal, New York City, the Chicago, Northwestern Terminal, Chicago, and the Central Railroad of New Jersey Terminal, Jersey City, N. J.

For the finish which it may be given as well as for its resistance to corrosion, Monel metal has been largely used for washing machinery, dairy equipment, cooking utensils, hotel, hospital and restaurant equipment, apparatus for the manufacture of food products, knives, golf heads, small fittings, trim and stampings.

Monel metal is resistant to erosion and retains much of its strength at high temperatures. It is used for these properties for turbine blading, gas-engine valves, seats and spindles in pressure valves, plugs in oil stills, etc. It will resist oxidation satisfactorily at temperatures up to 800°C., but should not in general be used at higher temperatures. Monel metal is used to some extent as resistance wire and as spark-plug electrodes.

**Copper-nickel-zinc Alloys.**—These alloys are known collectively as German silver or nickel silver. They are used in a wide variety of compositions and under various trade names for cutlery and table flatware, keys, jewelers' wire, brazing solder, watchcases, etc. For some uses, small amounts of lead or iron are added, but the general range of compositions falls within the limits, Ni, 5 to 30; Cu, 45 to 75; and Zn, 5 to 30 per cent. The alloys are white to slightly yellowish in color, malleable hot or cold, easily worked, and obtainable in the usual brass-mill shapes. They are also used in the form of sand castings. Manufacturer's recommendations should be sought for the correct alloy for any specific purpose.

These alloys take an agreeable finish and many are resistant to corrosion. Consequently, considerable quantities are used for ornamental castings and stampings, plumbing fixtures, and parts of food-handling apparatus. Some metal, in the form of wire, is used as a high-resistance metal in electrical work.

**Nickel-chromium Alloys.**—Nickel-chromium and nickel-chromium-iron alloys are very highly resistant to oxidation at high temperatures and to chemical corrosion, particularly under oxidizing conditions. They are malleable and are used

both in the wrought form for wire, etc., and almost entirely in the cast form for annealing boxes, carbonizing boxes, furnace parts, enameling racks, etc. These alloys have high electrical resistivity with low-temperature coefficients and are used in large quantities, as wire or ribbon, for heating elements in electrical apparatus and for other electrical properties. They are marketed under various trade names and range in composition as follows: Cr, 5 to 20 per cent; Fe, 5 to 40 per cent; Ni, balance.

**Nickel-steels and Nickel-iron Alloys.**--Nickel and nickel-chromium are the most widely used of alloy steels. Ordinary nickel-steel containing about 3½ per cent nickel is used for automobile parts, bridge and structural steel, die blocks, locomotive forgings and castings, machine and machine tool parts, ordnance, and power-plant equipment. These steels are used mainly in the heat-treated condition, in which form nickel refines the pearlite grain and increases hardness, yield point, and tensile strength without notably reducing ductility. Fatigue resistance and endurance under alternating stresses are increased and segregation is lessened. The addition of chromium to nickel-steels increases the beneficial effects of nickel and such steels are used to as great or greater extent than straight nickel-steels as heat-treated forgings for automobiles and other construction. More recently molybdenum nickel steels have come into general use.

Nickel steel of low-carbon content (0.1 to 0.2 per cent) is superior to carbon steel for case hardening both in uniformity of case and in mechanical properties of core after heat treatment.

The compositions of the most widely used nickel steels falls within the limit: Ni, 3.25 to 3.75; Mn, 0.5 to 0.8; and C, 0.1 to 0.5 per cent. Five per cent nickel steel is used for case-hardened parts to withstand particularly severe service conditions.

Nickel-chromium steels are described as low, medium, and high, and they range in composition as follows: Ni, 1.0 to 3.75; Cr, 0.45 to 1.75; and Mn, 0.30 to 0.80 per cent. The high nickel-chromium steels are used where particularly high physical properties are desired in all carbon ranges.

Nickel-iron alloys relatively high in nickel exhibit remarkable magnetic properties and wide variation in their thermal expansivity in normal temperature ranges. Many are also resistant to corrosion. Invar, 36 per cent nickel, has an extremely small coefficient of expansion at ordinary temperature and is used for measuring tapes, parts of precision instruments, etc.

Nickel and nickel-chromium cast iron is being used commercially today for rolling mill parts such as rolls, mill guides, pipe bending dies, pipe balls, etc., for automobile engines and other cylinder castings, for pistons and piston rings, for cast iron cams, for sheet and plate metal forming dies, in various thin section castings, prominently resistance grids—the amounts used varying from as little as 0.10 per cent (but usually not less than about 0.40 per cent) up to 5.0 per cent nickel and from 0 to 0.50 per cent chromium.

The principal useful effects of nickel and suitable nickel-chromium combinations in gray iron have proved to be: (1) To increase strength from 10 to 50 per cent, requiring 0.50 to 1.0 per cent nickel together with 0 to 0.50 per cent chromium depending on the grade of iron,—a higher silicon iron requiring a greater addition of chromium; (2) to increase hardness 20 to 50 points Brinell without impairing machinability, requiring similar amounts of alloy; or raising the hardness 100 points Brinell, with the iron still remaining machinable, but less readily so, with larger amounts of alloy; (3) to reduce edge, surface and corner chilling on thin sections or eliminate hard spots in castings made with comparatively hard iron and thus improve machinability;

requiring from 0.50 to 5 per cent nickel depending on conditions; (4) to increase toughness and deflection particularly of thin section castings by eliminating chill and hard spots, requiring also from 0.50 to 5 per cent nickel; (5) to refine grain and produce denser, less open castings requiring from .15 to 1.0 per cent nickel together with small amounts of chromium if desirable; (6) to equalize hardness and strength and machinability over large sections or between small, irregular sections.

Cast iron is itself a most complex and variable material and the use of these alloys in conjunction with it requires careful adjustment of the amount of the additions to the grade and composition of iron used as well as to the type and section of casting in question. Disappointing results may be obtained when alloy additions are made which are not suited to the particular conditions, and some tests have been made also on cast iron of high alloy content—up to 30 per cent nickel—and consideration is invited to their interesting and unusual properties as suited to special applications.

**Miscellaneous Alloys.**—Invar, a complex alloy of Ni and Cr with lesser amounts of Cu, Mo, W, Mg, Fe, Al, and Si, is very highly resistant to corrosion. It is practically unattacked in 25 per cent nitric acid solution.

Nickel-manganese, nickel-copper-manganese, and nickel-aluminum alloys are used in the form of resistance wires and as parts of pyrometer thermocouples.

Nickel has been added in small amounts to many other alloys of industrial importance, in which it acts chiefly to increase hardness without decreasing ductility. Light aluminum alloys, aluminum bronzes, and some brasses and bearing metals are to be noted in this connection.

Nickel alloys have been used as substitutes for platinum ware and so-called white gold is an alloy of nickel and gold.

A high-silicon nickel alloy in the form of shot and containing up to 5 per cent silicon is used for tumbling and burnishing purposes. It is harder than iron and does not rust.

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## CHAPTER XL

### TUNGSTEN, VANADIUM, URANIUM AND MOLYBDENUM

BY RICHARD B. MOORE<sup>1</sup> AND H. B. DOERNER<sup>2</sup>

**Introduction.**—Among the elements usually thought of as rare, vanadium, uranium, tungsten, and molybdenum stand out because of their importance in ferroalloys. These are, therefore, treated at length in this section.

#### VANADIUM

(Atomic weight = 51.0)

**Occurrence.**—Vanadium is never found free in nature. Its ores are fairly widely distributed, but seldom occur in quantity in any one locality. The principal ores are patronite, roscoelite, carnotite, vanadinite, cuprodesclowitzite, zinc desclowitzite, mottramite, and pucherite. Vanadium is found in small quantities in certain iron ores, and in the ash from lignites, coals, and other carbonaceous materials.

Patronite is an impure vanadium sulphide found in Minasragra, Peru. The composition is approximately  $V_2S_5$ , and it is associated to a certain extent with carbonaceous material, pyrites, and free sulphur. The area in which the ore lies is along the western limit of a broad anticline in "Jura-Trias" and Cretaceous rocks. A section shows the series in this locality to be composed of green shales, thin beds of limestone, and red shales. Vanadium is found only in the red shales. The deposit proper appears to be a lens-shaped mass, 28 ft. wide and 250 ft. long. The mineral that constitutes the larger portion of the deposit has been called "quisquete." It is a black carbonaceous substance containing sulphur, with a hardness of 2.5 and a specific gravity of 1.75. There is also a lesser quantity of a coke-like material with a hardness of 4.5 and a specific gravity of 2.2. Neither of these contain vanadium. The vanadium is mostly in the southern end of the ore body, and to a depth of 20 ft. is largely in the form of a red calcium vanadate, and carries as much as 50 per cent vanadic oxide. It occurs in pockets and fills the cracks and fissures in a fine shale.

Below this shale is the mother lode. It is from 9 to 30 ft. thick and extends along the greater length of the deposit. It carries as high as 10 per cent vanadic oxide and nearly as much sulphur. On the east and south sides below the mother lode is found a hard blue-black vanadium shale carrying as much as 13 per cent vanadic oxide and 4 to 5 per cent sulphur. Patronite, the main vanadium mineral, is greenish-black and has a hardness of 2.5 and a specific gravity of 2.71. It contains from 19 to 24.8 per cent vanadic oxide and sometimes 50 per cent of combined sulphur. This deposit in Peru constitutes the largest known source of vanadium at the present time and furnishes the Vanadium Corporation of America with its major supply of ore. As this

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<sup>3</sup> HAWERT, D. F., *Eng. Min. J.*, **82** (Sept. 1, 1906), 385; HILLEBRAND, W. F., *J. Am. Chem. Soc.*, **29** (1907), 1019.

company has been the largest producer of ferrovanadium and vanadium compounds in the world, patronite is by far the most important ore of vanadium from the commercial standpoint.

Roscoelite, or vanadium mica, is the second most important vanadium mineral commercially. It has a somewhat indefinite composition, the formula  $H_2K_2(MgFe)(AlV)_4(SiO_3)_{12}$  representing its composition fairly well. It exists in minute scales of a brown to greenish-brown color. Sometimes the color is actually green. The specific gravity is 2.92 to 2.94. It exists rather widely distributed in nature, but at only one place in the United States has it been worked commercially, namely, near Newmire, San Miguel County, Colorado.

Carnotite is mainly of importance on account of its uranium and radium content, but also carries usually from 3 to 5 per cent  $V_2O_5$  in ordinary commercial ores. It is found mainly in southwestern Colorado and eastern Utah, but also exists in smaller quantities in other localities, such as South Australia, Portugal, etc. It is a potassium uranyl vanadate of the following approximate composition:  $K_2O.2UO_3.V_2O_5.3H_2O$ . The crystals are canary yellow in color and usually exist as incrustations on other minerals, or are disseminated through a sandstone in which they are usually found. It also contains small traces of calcium and barium. Other deposits of vanadiferous sandstone similar to roscoelite or carnotite have been more recently discovered in Colorado and Utah; of these one near Rifle in Garfield County, Colorado, appears capable of considerable production. Another is reported in Emery County, Utah.

Vanadinite, or lead vanadate, is widely distributed, especially in certain of the western states of the United States, particularly Arizona, New Mexico, Nevada, and California. The largest deposits are in Arizona, where it is frequently associated with wulfenite, or lead molybdate. The deposits are almost always low grade and for this reason this mineral has not been used to any great extent as a source of vanadium in the United States. In Mexico, the vanadinite occurs at Villarosales, Chihuahua. In Spain, important deposits of vanadinite occur near Santa Marta, Estramaduras. The ore is found in a sandstone which contains on an average 3 per cent vanadic oxide. This can be concentrated, and these deposits supplied most of the vanadium used in the world up to the opening of the Peruvian mines. The mineral occurs in prismatic hexagonal crystals, and has a specific gravity of 6.6 to 7.1. It varies in color from ruby red to yellowish and even brown.

Cuprodesclowitzite is a hydrated lead-copper vanadate of the probable composition  $(PbCu)_2(OH)VO_4$ . Commercial samples of the ore may carry as much as 23 per cent  $PbO$ , 7 per cent  $CuO$ , and 8 to 10 per cent  $V_2O_5$ . The largest deposit of this mineral known at the present time is in the Shattuck mine at Bisbee, Ariz., although it is found in a few other localities in the United States.

Zinc desclowitzite is a mineral very similar to cuprodesclowitzite, where the zinc replaces the copper. It is found in Nevada, especially around Goodsprings, in New Mexico, in Arizona, and in Argentina. Mottramite, a vanadate of lead and copper, and pucherite, a bismuth vanadate, are of lesser importance to the minerals already described. Mottramite has been produced and shipped from Tsumeb, Southwest Africa.

**Extraction from the Ores.**—The method of extraction which can be used for vanadium ores varies materially with the ore and its grade. In general, a different metallurgical process must be used for every mineral treated, although there are, of course, some general similarities between the methods used.

Patronite is treated by first roasting in order to eliminate the sulphur as far as possible. It can then be leached with either sulphuric acid, filtered and the filtrate evaporated to a crude vanadic oxide, or the roasted ore can be leached with alkali—

sodium carbonate or caustic soda, which will dissolve the vanadium as sodium vanadate. From this a high-grade vanadic oxide can be obtained by acidifying with sulphuric acid, or after neutralization the vanadium can be precipitated as vanadate of iron by means of ferrous sulphate.

Roscoelite has been treated commercially at only one place in the United States, namely, at Newmire, Colo., where the Primos Chemical Co. had a mill (now controlled by the Vanadium Corporation of America). The method they used was to roast the ground ore with salt and a small percentage of ground pyrites. The ore contains almost no uranium, and no attempt was made to recover the minute quantity found in some of it. The mixed ore, salt, and pyrites were coarsely ground and run into a dryer, which reduced the moisture to 1 per cent. The material which came out somewhat caked was ground to 20 mesh and roasted in a furnace for about 3 hr. The roasted material was delivered at the bottom of the furnace to conveyors which carried it to lixiviation tanks, where it was treated with water and filtered. The vanadium was now in solution as sodium vanadate. A solution of ferrous sulphate was added, and the vanadium was precipitated as vanadate of iron. This precipitate was filtered out of the solution and partially dried and shipped to the company's reduction works. Roscoelite is not very amenable to acid-leaching methods, as the mineral is quite insoluble. G. A. Koenig<sup>1</sup> claims, however, that the mineral can be decomposed by either dilute sulphuric acid or hydrochloric acid under proper treatment as regards both heat and pressure. In practice, he proposes to use a solution containing 20 per cent sulphuric, hydrochloric, or other acid at a temperature of about 200°C., and under a pressure of 225 lb. per square inch; and he claims that this process will completely decompose and dissolve the roscoelite within a few hours.

Carnotite is almost exclusively treated for its radium content, and practically all metallurgical processes for the treatment of carnotite have in view the extraction of the radium primarily, while the recovery of the uranium and vanadium is of secondary importance. Some processes, therefore, do not obtain a high recovery of the vanadium. Metallurgical methods for the treatment of carnotite are discussed more fully in the chapter on Radium, and under Uranium in this section.

These methods may be classified by their initial operation as (1) acid leach; (2) digestion and extraction with sodium-carbonate solution (usually with some free caustic); (3) bisulphate (niter cake) fusion; (4) other sintering or fusion treatments. Of the acid methods, sulphuric gives the best extraction of vanadium, hydrochloric is also good, but nitric acid is very inefficient and requires a subsequent alkaline leach. Sodium carbonate solution also gives a poor extraction of vanadium even at autoclave temperatures. Fusion with niter cake, followed by a water leach, extracts the vanadium completely. Alkaline fusions may also give high recoveries, but are unsatisfactory because of furnace-lining and filtration difficulties.

From a soda solution, uranium is precipitated by sodium hydroxide after neutralizing the carbonate. The vanadium is obtained by neutralizing the filtrate from the uranium and adding either a slight excess (1/20 N) of sulphuric acid and boiling to precipitate vanadic acid, or adding a metal salt (ferrous sulphate, calcium chloride) to form the corresponding vanadate. From an acid leach, vanadium is precipitated with uranium and a portion of the basic elements present by carefully neutralizing and boiling. When sulphuric acid is present in large excess, it is economical to neutralize most of it with lime or limestone and filter off the calcium sulphate before precipitating the vanadium. In some cases the vanadium precipitate is reduced to ferro-alloy, but usually additional refining is necessary. This may be accomplished by extracting the precipitate with hot soda solution and precipitating as previously described for alkaline solutions.

<sup>1</sup> U. S. patent 986180.

Vanadinite was originally treated by leaching with sulphuric acid. This dissolved the vanadium and left the lead as insoluble lead sulphate, from which the lead could be recovered by smelting. The process was not a success, because the action stopped after a short time, owing to the crystals of the vanadinite being coated with the lead sulphate, which prevented further action. J. E. Conley has thoroughly studied the treatment of vanadinite.<sup>1</sup> The method recommended by him is to fuse the vanadinite concentrate with a mixture of soda ash and caustic soda, which gives a better melt and a better recovery than soda ash alone. The lead is recovered as metallic lead and the vanadium is precipitated by means of slaked lime, giving calcium vanadate as a product. If any trace of molybdenum is present, the latter metal does not come down with the vanadium and is thus eliminated. The calcium vanadate can be treated with sulphuric acid, the precipitated calcium sulphate filtered off, and the vanadium recovered as high-grade vanadic oxide.

Cuprodesclowitzite has never been treated commercially, but, as it constitutes an important and potentially fairly large source of vanadium, Conley's method is of interest.<sup>2</sup> The object is to recover the lead, copper, and vanadium. Conley found that a sulphuric acid leach gives a fairly satisfactory extraction, but his preferable method is to subject the ore to a preliminary fusion with niter cake, followed by a hot-water leach, and then treat the residue with sulphuric acid. By heating the ore with an equal weight of niter cake, approximately two-thirds of the ore can be decomposed and the corresponding values extracted. The remaining values are then extracted by leaching the residue with about one-half as much acid as is required in a straight-acid treatment.

Zinc desclowitzite up to the present time has not been treated commercially. The principal deposits in Nevada carry considerable quantities of calcite, which make an acid treatment expensive and, therefore, undesirable. Doerner<sup>3</sup> has shown that a more economical method is the fusion of zinc desclowitzite concentrate with carbon, caustic soda, and soda ash to convert the vanadium to water-soluble sodium vanadate and separate the lead and precious metals as bullion. The vanadium is leached from the slag, acidified with sulphuric acid, and precipitated as vanadic acid by boiling with steam.

Most vanadium ores are not readily amenable to concentration. Patronite is partially concentrated by roasting. Roscolite was never concentrated at Newmire, Colo., the ore being treated direct. The writers, however, know of one gold ore in California containing roscolite from which a high-grade vanadium concentrate has been obtained during the concentration of the ore for gold. Carnotite has been concentrated by both sliming and dry concentration, *i.e.*, attrition and dusting. Preliminary roasting increases the extraction, especially with carbonaceous ores. Vanadinite is easily concentrated by the usual methods involving tables and sliners. It is, however, difficult to separate vanadinite from wulfenite, a mineral with which it is frequently associated, owing to the fact that both minerals have almost the same specific gravity. Cuprodesclowitzite and zinc desclowitzite will also concentrate on tables and slimers, but no commercial plants are known to the writers. The main difficulty is a high loss in the slimes.

**Metallic Vanadium.**—Metallic vanadium has been produced by Gin<sup>4</sup> by the electrolysis of a solution of vanadium trioxide in fused calcium vanadate. The material may also be prepared by the aluminothermic method, and by reducing the dichloride in hydrogen, in which case the metal is a light whitish-gray powder.

<sup>1</sup> *Chem. Met. Eng.*, **20** (No. 10), 514.

<sup>2</sup> *Chem. Met. Eng.*, **20** (No. 9), 465.

<sup>3</sup> U. S. Bur. Mines, *Rpt. of Investigations* 2433.

<sup>4</sup> *Electrochem. Met. Ind.* (1909, No. 7), 264.



The metal has a hardness greater than that of steel or quartz. It takes a good polish and is not affected by air. If the powdered metal is thrown into a flame, or rapidly heated in oxygen, it burns brilliantly. Its specific gravity at 15° is 5.5.

**Ferrovandium.**—As the principal use of vanadium is in steel and as the vanadium is always added to the steel in the form of ferrovandium, the manufacture of the latter product is of great importance. Formerly, 75 per cent of the ferrovandium produced in this country was made in the open-hearth or crucible furnace by a modification of the thermit process, using aluminum as a reducing agent.<sup>1</sup> The remainder was produced by the electric furnace, using 90 per cent silicon as the reducing agent. Recently, the difficulties of reduction with carbon in the electric furnace have been surmounted,<sup>2</sup> thus eliminating expensive reducing agents.

A satisfactory ferrovandium for commercial purposes contains from 30 to 40 per cent vanadium and not more than 0.5 per cent C, 1 per cent Si, 2 per cent Al, 0.1 per cent S, and 0.1 per cent Ph. It has a good fracture, is not crystalline, and is bright gray in color. Too much carbon is injurious, because it makes a carbide with the vanadium, which is not satisfactory in steel making. In the aluminothermic or Goldschmidt method, vanadium oxide or iron vanadate is reduced with aluminum shot in a gas-fired open-hearth furnace, slagging off the alumina by the addition of soda ash or fluor spar. When the oxide is used, iron turnings must also be added. The process is exothermic, but it is sometimes necessary to apply external heat in order to maintain the temperature required for a fluid melt. This may also be accomplished by adding oxidizing agents, such as niter, intimate mixing, and rapid rate of feed, with large scale of operation. The use of iron vanadate requires more aluminum than the oxide. When applied to complex ores, this method presents great difficulties, as the charge must be calculated so as to eliminate all undesirable elements in the slag and at the same time produce a good recovery of high-grade alloy and the proper amount of heat.

Silicon or ferrosilicon gives a satisfactory reduction in the electric furnace. The raw materials required are steel turnings, vanadium oxide, silicon, lime, and fluor spar. If iron vanadate is used, the steel turnings are not added. All material should be low in phosphorus, but sulphur can be eliminated with the slag by remelting.

In the method developed by Saklatwalla for electric-furnace reduction with carbon, the ore-flux mixture is fed continuously into a localized zone of extremely high temperature, which is obtained by high voltage and current density, combined with close spacing of the electrodes. In this way the vanadium is supposed to be reduced directly from the pentavalent form to the metal, without the intermediate formation of the infusible and insoluble lower oxides which caused trouble in previous attempts. The furnace is three-phase, rectangular, with water-cooled bushings for three 12-in. graphite electrodes. It is automatically charged through water-cooled bushings in the cover.

The melting point of ferrovandium, practically free from other elements and containing 40 per cent vanadium, is about 1480°C. The melting point becomes gradually lower as the amount of vanadium is decreased until 35 per cent is reached, when it melts at 1425°C, and remains stationary until the alloy contains 30 per cent. At this point the melting point gradually rises to about 1450°C.

**Uses of Vanadium.**—The chief use of vanadium is for making vanadium steel. The general effect of this rare element on steel is to increase the elastic limit and

<sup>1</sup> *Bull. A. I. M. E.* (August, 1919), 1342

<sup>2</sup> *SAKLATWALLA, J. Ind. Eng. Chem.*, 14 (No. 10), 968.

tensile strength without reducing the ductility. It is usually alloyed with chromium or manganese to give chromium-vanadium or manganese-vanadium steel, and is also used in open-hearth and high-speed tool steels. Vanadium is found in much of the steel used in motor cars, locomotive axles, rock drills, etc. The metal causes oxides and nitrides present to pass into the slag, and a certain portion of it also goes into solid solution, rendering the metal more coherent and less liable to disintegration. The quantity of vanadium added to steel is small, the amount usually being between 0.1 and 0.4 per cent.

Other uses for vanadium are as alloys with copper and aluminum. These alloys make excellent castings. It has been used in photography for toning silver bromide plates to a green color. Vanadium salts have also been used in pottery and glass, and as mordants.

The chemical activity of vanadium and the large variety of its compounds will probably lead to a much wider chemical use. Vanadium pentoxide has been proposed as a catalyst in the synthesis of ammonia and also in the oxidation of sulphur dioxide. The catalyst is prepared by heating briquettes made of 10 parts alumina and 1 part ammonium vanadate.<sup>1</sup>

**Analytical Methods for Vanadium.**—Vanadium in an ore can be recognized qualitatively in the following manner: The ore is ground and boiled with hydrochloric acid, filtered, and to the cold acid solution hydrogen peroxide is added. A deep-red color indicates the presence of vanadium. In a mineral such as roscoelite, which is with difficulty soluble in hydrochloric acid, the ore should be fused with sodium carbonate, leached with water, filtered, and the filtrate made acid with hydrochloric acid. On adding hydrogen peroxide, the red color will then be obtained. The choice of a quantitative method will depend upon the ore, or vanadium compound, to be analyzed. Full analytical details are given in U. S. Bureau of Mines *Bull.* 70 and 212. The following method is quick and applicable to a large variety of vanadium ores, especially those which contain little insoluble material and are decomposed by acids. Weigh out a 1-g. sample of the pulverized ore and add 25 c.c. of concentrated hydrochloric acid. Heat on a hot plate to a small volume, then add 10 c.c. of concentrated nitric acid and continue heating until decomposition is complete. Remove from the hot plate, cool, and dilute to about 25 c.c. Now add 10 c.c. of concentrated sulphuric acid and heat to copious fumes.

Cool slightly and carefully add about half a gram of potassium permanganate. Again heat and cool, then add 5 c.c. of water and 10 c.c. of hydrochloric acid and evaporate to copious fumes of sulphur trioxide. Repeat with two more evaporations of 5 c.c. of hydrochloric acid. Cool and dilute to about 150 c.c., warm to dissolve the ferric sulphate, and then titrate at 70 to 80° with N/20  $\text{KMnO}_4$  to a pink which persists for half a minute. It is advisable to run a blank determination, which usually requires from 0.4 to 0.5 c.c. of N/20  $\text{KMnO}_4$ . Fe factor  $\times 1.63 = \text{V}_2\text{O}_5$ . In an insoluble mineral, such as roscoelite, it is advisable to filter off the insoluble material and to treat with hydrofluoric and sulphuric acids in the usual manner to eliminate the silica, and then to redissolve in a mixture of hydrochloric and nitric acids. The method is applicable in the presence of large amounts of iron; molybdenum does not interfere; and arsenic, if present only in small amount, may be overlooked. Large amounts of arsenic, however, should be removed by first passing sulphur dioxide through the solution after evaporating the first time to sulphur trioxide fumes, boiling

<sup>1</sup> U. S. patents 1420201 to 1420203.

was attempted, the uranium in the alloy oxidized and went into the slag, leaving pig iron in the furnace. Keeney<sup>1</sup> was unable to get a ferrouanium containing as much as 30 per cent uranium, and, in addition, the carbon content was too high. He was, however, able to get a commercially high-grade uranium metal as described above. Gillett and Mack<sup>2</sup> succeeded in making a satisfactory ferrouanium by using a pure  $\text{UO}_2$ , a low-ash coke, and a pure iron as raw materials, with calcium fluoride as slag former. They stated that, by using a tilting direct-arc type furnace with water-cooled magnesite hearth and sides, it should be possible to produce commercially, without a second refining operation, ferrouanium of any desired uranium content, say 40 to 70 per cent, with C averaging below 2 per cent, Si below 0.75 per cent, V below 0.5 per cent, and with Al, S, P, and Mg all so low as to be negligible.

**Uses of Uranium.**—Besides its use in steel, uranium has been used for many years as a coloring agent for glass. Sodium uranate is usually desired, although uranium oxide is sometimes used as a substitute. The color produced is opalescent yellow, turning green by reflected light. Usually about 20 per cent of uranium calculated as oxide is required to produce the color, thus making the glass quite expensive. Uranium salts are also used in the ceramic industry, and produce yellow, orange, and black glazes. The coloring power is great and only small quantities are required. Uranium salts have also been used to some extent as mordants for silk and wool, and also as a catalyst in the synthesis of ammonia from nitrogen and hydrogen.<sup>3</sup> In photography, uranium nitrate has been used as a sensitizing agent for paper. With potassium sulphocyanide it can be used for toning bromide prints.

Since Keeney and Gillett made ferrouanium and commercial uranium metal, some interest developed for a time in connection with uranium steel. One firm in this country had ferrouanium on sale and actively cooperated with one or two steel manufacturers in the manufacture of uranium steel. One part of uranium is supposed to replace from 2 to 3 parts of tungsten in high-speed steels. Keeney<sup>4</sup> states that ferrouanium can be added to steel in quantities up to 4 per cent with a uranium recovery of at least 50 per cent; and a recovery of 70 per cent can be made in steel containing less than 2 per cent uranium. A considerable portion of the carbon and silicon in the ferrouanium seems to enter the steel. For a steel containing less than 2 per cent uranium, the ferrouanium can be added in the ladle, but a higher percentage of uranium in the steel requires addition in the furnace, or chilling will occur. These results were obtained in the electric furnace, but uranium can also be made in the crucible furnace. Uranium steel has not come into general use, although some of the steel makers have claimed that uranium is a satisfactory substitute or tungsten in certain cases.

**Analytical Methods for Uranium.**—A number of methods are suitable for the analysis of uranium ores, and these are discussed at length in *Bull.* 212 of the U. S. Bureau of Mines. The following short method is usually satisfactory.

Take a 2- to 5-g. sample, ignite if it is carbonaceous, add 16 c.c. of 1:1 sulphuric acid, and a few drops of nitric acid and heat till fumes of sulphur trioxide appear. Cool, dilute to 100 c.c., add an excess of sodium carbonate and hydrogen peroxide,

<sup>1</sup> *Bull. A. I. M. E.* (August, 1918), 1353.

<sup>2</sup> *J. Ind. Eng. Chem.*, 9 (1917), 432, U. S. Bur. Mines, *Tech. Paper* 177.

<sup>3</sup> HABER and LE ROSSIGNOL, *Z. Elektrochem.*, 19 (1913), 53.

<sup>4</sup> *Bull. A. I. M. E.* (August, 1918), 1366.

boil 10 min., filter, and wash with hot water. The iron precipitate should be washed back in the beaker, digested with fresh soda solution, and refiltered, combining the filtrates, which are then acidified with sulphuric acid. After boiling off all  $\text{CO}_2$ , 2 g. of ammonium phosphate are added, the solution is made slightly alkaline with ammonia, and then barely acidified with acetic acid. The precipitate is gently boiled for 10 min., filtered, and washed thoroughly with a hot 2 per cent ammonium sulphate solution. For accurate work, the precipitation may be repeated. Dissolve the precipitate in 1:4 sulphuric acid and wash to a volume of 100 c.c. Add an excess of potassium permanganate and 10 c.c. sulphuric acid and after warming a few minutes add 5 g. of granulated zinc. Reduce hot for 10 min., cool, filter through glass wool, washing to a volume of 250 c.c. with cold water. Titrate with twentieth normal permanganate. The iron value of the permanganate times  $2.5176 = \text{U}_3\text{O}_8$ .

### TUNGSTEN

(Atomic weight = 184)

**Occurrence.**—There are four reasonably common tungsten minerals found in the United States. Ferberite, wolframite, and hübnerite are closely associated as regards their composition. Ferberite is usually classed as an iron tungstate, although it may and often does carry moderate quantities of manganese. Wolframite is an iron-manganese tungstate, carrying usually, however, more iron than manganese. Hübnerite is a manganese-iron tungstate containing more manganese than wolframite. These minerals form a complete series with almost an infinite number of members between a pure iron tungstate and a pure manganese tungstate. Scheelite, calcium tungstate, is the fourth.

Hess<sup>1</sup> has suggested the following definitions: "Ferberite should be considered as an iron tungstate ( $\text{FeWO}_4$ ) contaminated by not more than 20 per cent  $\text{MnWO}_4$ , a proportion equivalent to 4.69 per cent  $\text{MnO}$ , or 3.63 per cent Mn in the pure tungsten mineral. Hübnerite should be considered as manganese tungstate ( $\text{MnWO}_4$ ) contaminated by not more than 20 per cent  $\text{FeWO}_4$ , a proportion equivalent to 4.74 per cent  $\text{FeO}$ , or 3.69 per cent Fe. Wolframite should cover the ground between the limits above indicated. That is, wolframite should be considered a mixture of iron and manganese tungstates containing not less than 20 per cent nor more than 80 per cent of either. Except the light-colored hübnerites, most of these minerals cannot be detected by the eye or by simple tests, and in the absence of analyses it is, therefore, convenient to refer to the dark minerals of the series as wolframites." Ferberite and wolframite, when pure, are black. When partly oxidized they may appear brownish from the presence of iron oxide. Hübnerite is characteristically brown, some specimens, however, being yellowish, others reddish, and some nearly black. These minerals are all monoclinic in form. Ferberite has more of a tendency to form well-defined crystals than do the others. In hardness, all of these minerals are a little over 5. Their specific gravities range from 7.2 or 7.3 in hübnerite to 7.5 in ferberite, while the specific gravity of wolframite is intermediate between these figures. Scheelite is a calcium tungstate ( $\text{CaWO}_4$ ). In color it is usually white, light gray, or light yellow, although its color may occasionally vary from greenish yellow to brown. Its luster is slightly glassy. It is found in granular masses, or in irregular lumps of a more or less coarse texture. Its hardness is a little less than 5, and its specific gravity is approximately 6. It possesses four directions of good cleavage. Other tungsten minerals of less importance are stolzite or lead tungstate, cuprotungstite or hydrated copper tungstate, and tungstite or tungstic ocher, a hydrated tungstic oxide.

<sup>1</sup> U. S. Geol. Survey Bull., 652, p. 22.

Ferberite is found in several western states, but mainly in Colorado in the Boulder district. This district has a length of 12 miles in a northeast and southwest direction, and a width of about 7 miles, and begins about 6 miles due west of the town of Boulder. The tungsten veins are in many ways similar to the gold veins of the district, and seem to have a close connection with them in genesis. Hübnerite and wolframite are mainly found in New Mexico, Arizona, Nevada, and South Dakota, although the minerals are frequently met with in small quantities in other states. They do not form so important a commercial source of tungsten as ferberite and scheelite. The latter mineral is mainly found in California, principally near Atolia in northwest San Bernardino County. A second area of considerable importance lies in Inyo County, near Bishop. The Atolia-Randsburg district occupies an area of about  $2\frac{1}{2}$  by 10 miles in extent. Tungsten minerals are found to a very considerable extent in foreign countries, namely, in Burma, Siam, the Malay States, Portugal, Bolivia, Argentina, Peru, England, China, Australia, and New Zealand. During the last few years, ores from these countries have competed to a very considerable extent with United States ores.

**Extraction from the Ores.**—Up to recent years, most methods of treatment of tungsten ores were small modifications of the original Oxland process, which was patented in 1847. This involves a fusion with sodium carbonate of the finely ground ore previously leached with hydrochloric acid to get rid of traces of bismuth if this metal is present. Sometimes a small amount of sodium nitrate is added to the sodium carbonate. The mixture is placed in a reverberatory furnace and sintered, care being taken not to fuse it. It is then removed and ground. Frequently, this treatment does not give a sufficiently high extraction of the tungsten, and involves a second sintering process. The sintered mass is leached with hot water in tanks. Tungsten dissolves as sodium tungstate, while the iron, calcium and most of the manganese remain insoluble. Some of the phosphoric acid and silicic acid also dissolve as silico- and phosphotungstates. Traces of manganese may also dissolve, owing to the sodium nitrate present, as sodium manganate. The solution of sodium tungstate may be either evaporated to dryness, or evaporated to the point at which crystallization takes place. The chief impurities are sulphates, silicates and arsenates of sodium, with traces of iron and manganese. Iron, manganese, and arsenic are precipitated by a small quantity of caustic soda, and the greater portion of the sodium sulphate will crystallize out before sodium tungstate. The silica remains in the mother liquor, after the crystallization of the sodium tungstate, and causes some loss of tungsten in the form of soluble silicotungstates, which, however, can be used as by-products for fireproofing purposes. The fairly pure sodium tungstate is redissolved in boiling water and added to a boiling solution of hydrochloric acid made up of 1 part of concentrated acid and 7 of water. Sometimes about 5 per cent of nitric acid is added. The result is the precipitation of the tungsten as hydrated tungstic oxide, which is filtered off and washed in filter presses. It is important that the oxide should be washed free from sodium salts, as otherwise on drying it has a greenish tinge which is not attractive to purchasers.

One of the best methods, if not the best, for producing a high-grade tungstic acid is that of Ekeley and Stoddard.<sup>1</sup> This process is used at one mill in Boulder County for the treatment of medium-grade ferberite ores and concentrates. Usually middlings from the mills, or ore running from 15 to 25 per cent  $\text{WO}_3$ , are used. The

<sup>1</sup> U. S. patents No 1255144 and 1322485

product is a high-grade tungstic acid, said to contain less than 0.03 per cent phosphorus and 0.03 per cent sulphur, with only a small per cent of silica. After drying, the oxide runs from 99 to 99.7  $\text{WO}_3$ . The ore is mixed with sodium carbonate and salt and the charge is placed in sheet-iron pans 2 by 4 ft. and 6 in. in depth. This is placed in a fire-brick furnace heated by oil burners. The charge is so proportioned that a glass slag is obtained. The heat treatment requires about an hour, at the end of which the pans are pulled out of the furnace onto an iron rack, clamped, and inverted, and the fused charge dumped into an iron receptacle, where it is allowed to cool. It is broken into pieces and ground in a crusher to approximately  $\frac{1}{2}$ -in. size. It is then mixed in a cement mixer with a hot-water wash liquor from a previous run. The contents are dumped into a screen-bottom trough, which retains the coarse residue. This is shoveled back into the mixer and washed with hot water, the wash water being used in the next run. The concentrated solution is allowed to settle and the clear solution is given a secret treatment, which removes the last traces of the phosphorus, arsenic, silica, and other deleterious substances. This probably involves the use of magnesium chloride as a precipitant. After filtering, the clear solutions are run into a large wooden tank, heated, and calcium tungstate is precipitated by the addition of a solution of calcium chloride. The precipitate is allowed to settle, and is scraped out and treated with commercial hydrochloric acid in a wooden revolving drum. After settling, the solution is drawn off through suction filters. The residue is treated twice with hydrochloric acid in this manner, and finally the whole is dumped onto the suction filters. This treatment produces tungstic acid as a precipitate, and the acid solution contains calcium chloride and calcium sulphate. This is allowed to run into stone vessels, in which the calcium sulphate crystallizes out, and the clear solution is drawn off into barrels, to which lime is added, which produces calcium chloride for further use.

Acid-leaching methods are also used in connection with all the commercial tungsten ores. They are especially used for getting rid of manganese, and give good results with scheelite. Ferberite, wolframite, and hübnerite are soluble in hot concentrated hydrochloric acid, but it is necessary to digest the ores in the acid for a considerable time. Under such conditions the ores are decomposed and the manganese goes into solution, while the tungsten is precipitated as tungstic acid and remains with the insoluble residue. After filtering, the residue is extracted with ammonia, which dissolves the tungstic acid, giving ammonium tungstate. On ignition, this is decomposed, giving tungstic acid and ammonia, which may be recovered for further use. Phosphorus is gotten rid of at some stage in the operation by precipitating with magnesium chloride, or, if tungsten powder is made from the tungstic acid, a considerable amount of phosphorus can be leached out of the powder with hydrochloric acid. Scheelite is soluble in hydrochloric acid, but one firm adds to the ease of solubility by using hydrochloric acid and sodium chlorate. The decomposition of the ore takes place in acidproof earthenware pots in a hood with a steam draft. After complete decomposition the tungstic acid and insoluble silica are filtered off. By using high-grade scheelite the amount of silica present is not large, and the refining of the product is not carried any further, but the acid, without further removal of the silica, is used for the manufacture of tungsten powder.

Gin<sup>2</sup> suggests a bisulphate fusion for the ore whenever tin is present. This method, therefore, does not apply specially to American ores, but is useful for some of the foreign ores. The tin can be largely separated from the tungsten ore by means of magnetic separation, but there is usually at least 1 per cent of tin oxide left behind with the tungsten. The ore is decomposed by means of acid potassium sulphate in a muffle furnace. After the sulphate is fused, the ore is thrown in and the mass is stirred continually and the temperature increased until the whole mass is fluid enough

<sup>2</sup> *Trans Am Electrochem Soc*, 12, 481.

to run out of the furnace. After solidification the fused mass is ground and treated with water, which dissolves the soluble sulphates and phosphoric acid and leaves insoluble potassium acid tungstate as a white amorphous precipitate. About 50 per cent excess of bisulphate over that theoretically required is actually necessary. The insoluble residue is dried and treated with a warm solution of ammonium carbonate, or cold ammonia water in which carbon dioxide is passed. The potassium acid tungstate dissolves leaving the silica, the cassiterite, and the insoluble sulphates. The solution is evaporated to crystallization, which gives ammonium tungstate, from which tungstic oxide is made by heating.

**Concentration Methods.**—The tungsten minerals are all very amenable to concentration methods, the methods used involving jigs, tables, and slimers. A good many mills also have "rag plants," instead of slimers, or work the two together. The average grade of concentrate that was demanded up to five or six years ago was around 60 per cent. Since 1918, concentrates of 55 per cent were classed as high grade. One of the difficulties in connection with milling operations is the handling of second-jig and low-grade slime products. These to a certain extent have been taken care of by a chemical treatment plant. Where this is not used, the product, of course, is often reground and reconcentrated, but this always involves considerable loss. Mill operations have been improved very much during the last eight years, and an average recovery of 85 to 87 per cent is not now uncommon.

**Metallic Tungsten.**—Metallic tungsten can be made in a number of ways. The purest product is obtained by heating a very high-grade tungstic oxide in a current of hydrogen. The oxide can also be reduced by means of carbon or metallic zinc. Metallic aluminum and magnesium also can be used instead of zinc. Most metallic tungsten prepared commercially is in the form of powder for making tungsten steel. Reduction with carbon is the method usually used, as the reaction goes readily and presents few difficulties. The reduction can take place either in a steel tube or in a covered steel crucible. Davis<sup>1</sup> has carefully studied the conditions and temperatures necessary for the reduction of tungstic oxide to the metal. He finds that at 650 to 850° the oxide goes to a black or purple on heating with carbon; at 950 to 1050°C. a chocolate-colored product is the result (probably  $WO_2$ ); and at temperatures above 1050°C. the gray, powdered, metallic tungsten results. The ratio of tungstic oxide to carbon varies from 10:1 to 10:1.6, depending upon the process used, the temperature of reduction, and the time involved. A small excess of carbon can be partially removed by washing. Both fire-clay crucibles and iron tubes give satisfactory results, and a product of over 98 per cent metallic tungsten can be produced. Whereas the reduction to metal is complete at 1050°C., it is better to keep the temperature around 1100°C.

Shapley's process for producing commercial tungsten is thus described:<sup>2</sup> A scheelite concentrate is mixed with crude soda (trona) in a ball mill, and the batch transferred to a fire-brick crucible and melted with crude oil fuel, the flame striking directly on the charge. When the melt is quiet, the charge is tapped, the molten material flowing directly into a small Pachuca tank nearly filled with water. The water is agitated violently by compressed air during the pouring of the charge and for an hour

<sup>1</sup> *Jour. Ind. Eng. Chem.*, 11 (No 3), 201.

<sup>2</sup> *Chem. Met. Eng.*, 24 (Mar 2, 1921) 374.

in addition. The action of the water on the molten sodium tungstate shatters this material so that it will all pass a 20-mesh screen and the sodium tungstate is easily and completely dissolved. The charge from the Pachuca is transferred to a redwood filter tank having a filtering medium of coco matting and canvas. The filtrate runs to storage tanks through a small filter press having filter paper between the plates. An absolutely clear solution results and, as the amount of insoluble matter is small, the press is cleaned only at rare intervals. The material in the filter tank is washed several times and the wash water returned to be used for the next melt.

To precipitate an easily filterable tungstic oxide, the solution is brought to boiling by means of steam coils placed directly in the solution and the boiling solution is transferred to stoneware crocks. The crocks are jacketed for hot water and contain enough hydrochloric acid to precipitate the tungsten as oxide. (About 3 per cent of nitric acid is used with the hydrochloric.) If the solution is kept nearly at the boiling point, the precipitate will be comparatively coarse grained and easily filtered.

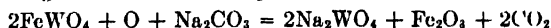
The precipitated material is allowed to stand for an hour at a temperature close to 100°C., and the clear, weak acid solution decanted and replaced with distilled water obtained from the heating coils. The precipitate is run into a flat-bottomed filter tank having a filtering medium of coco mat and canvas (protected with shoveling strips) and is washed repeatedly with distilled water. An acid-free product results, containing about 45 per cent water, as determined by heating a sample to 500°C.

The batch is then transferred to a wooden mixer similar to a butter churn, and the correct amount of gas-house carbon is added to reduce the tungsten oxide to the metal. After kneading for half an hour the mixture is transferred to fire-clay crucibles and allowed to dry slowly, waste heat from the reduction furnace being used to dry the product completely. Any reduction in volume due to shrinkage during drying is made up with more dry material, and the crucibles are covered with a graphite lid, ground to fit.

Reduction is done in a special furnace, which is operated continuously and reduces a charge in about a 4-hr. heating at 1250°C. Fuel oil is used for heating the furnace.

The metallic tungsten is a lumpy gray mass that must be ground and screened, and packed in 100-lb. tins.

The process used by the Fansteel Products Co. uses a hand-picked wolframite ore which is charged in a small reverberatory, 200 lb. ore to 100 lb. soda ash. The charge is hand rabbled at 800°C., which converts all manganese oxide to dioxide, while the following main reaction takes place:



The temperature must be kept low enough not to fuse the mass. The furnace bottom is now a 1-in. iron plate, but basic brick are recommended.

The furnace product is leached, and the sodium tungstate solution at from 30 to 50°Bé. is brought to boiling and 20°Bé. calcium chloride solution added. The calcium tungstate thus produced is washed by decantation and is then boiled by means of live steam with hydrochloric acid, thus producing tungstic acid.

This tungstic acid is then converted to ammonium paratungstate and the ammonia removed by nitric acid. Reference to the original article should be made for details of this process.<sup>1</sup>

Davis also found that the temperature of reduction with hydrogen at ordinary pressures is much the same as with carbon. The properties of metallic tungsten are unique, so that when it was first prepared it led to a search for methods for producing the metal in a ductile form. It was found that this could be done by repeated heating, rolling, hammering, drawing, and swaging. Cast tungsten, or tungsten powder, differs widely in its properties from the pure raw material, such as is used in the manu-

<sup>1</sup> *Chem Met Eng*, 22 (Jan 7, 1920), 9



fracture of incandescent-lamp filaments. The tungsten powder is brittle, crystalline, and hard and has a specific gravity of 16 to 17. The pure metal is softer and tougher, can be welded at a yellow heat, and even drawn into fine wire. Its specific gravity is 19.3 or over, and the melting point close to 3270°C. A wire of 5-mm. diameter has a tensile strength of more than 450,000 lb. to the square inch. At a red heat, the metal oxidizes in the air. Melted sulphur and phosphorus attack it slowly; potassium bisulphate, caustic alkalis, and fused nitrates attack the metal, but solutions of these salts have practically no action on it. Hot dilute sulphuric acid affects it only slightly, but the concentrated acid dissolves the metal slowly. At ordinary temperatures hydrochloric acid of any concentration has practically no action, but the strong boiling acid dissolves it slowly. Concentrated nitric acid and hydrofluoric acid have very little action on tungsten, but the two acids when mixed attack it fairly rapidly.

**Ferrotungsten.**—Tungsten is the principal rare metal used for alloy purposes in connection with the manufacture of high-speed steels. In making this steel, either ferrotungsten or tungsten powder may be used. The annual production of the two is probably about equal in quantity. When ferberite is used, practically all ferrotungsten is made directly from the high-grade concentrate without previous chemical treatment of the ore. The product obtained in such a case contains usually from 70 to 85 per cent W, 0.5 per cent C, 0.4 per cent Si, 0.5 per cent Mn, 0.01 per cent S, and 0.02 per cent P. Ferrotungsten has a high density, a fine gray fracture, and is not crystalline.

Keeney<sup>1</sup> gives a detailed description of the manufacture of ferrotungsten. The reduction with carbon goes readily. The slag may contain as high as 8 per cent FeO, but less than 1 per cent WO<sub>3</sub>. Theoretically, the reduction of 100 parts of alloy from 122 parts of ferberite requires 16 parts of carbon, but practically about 25 per cent excess of carbon is charged. Small amounts of lime and fluor spar are used to flux the silica. Operating in this manner, with an excess of carbon, a product is made containing 3 per cent C, 70 per cent W, 0.05 per cent P, and 0.01 per cent S, with slag containing below 1 per cent WO<sub>3</sub>. The analysis of a typical concentrate for the manufacture of such a product is WO<sub>3</sub>, 60.36; Fe, 22.0; SiO<sub>2</sub>, 8.0; Mn, 0.05; S, 0.35; and P, 0.05 per cent.

A typical operation involves charging into the furnace 65 lb. of a mixture composed of 200 lb. concentrate, 42 lb. coke, 56 lb. lime, and 6 lb. fluor spar. Three more 65-lb. charges are added at intervals of ½ hr., and at 2½ hr. from the start the furnace is tilted and the slag poured. This cycle is repeated until a 1,200-lb. button has been formed, requiring 24 to 36 hr. The furnace is allowed to cool, is torn down, and the button of metal removed, cleaned, and broken up. This crude metal is refined as follows: A charge of 150 lb. metal and 75 lb. ferberite concentrate are smelted for ½ hr., when 12 lb. of fluor spar are added. After another 3 hr. the slag is poured and a fresh charge is started. The process is continued for from 36 to 48 hr. until a button weighing 1,500 lb. has been formed, when the furnace is allowed to cool, is torn down, and the button of metal removed, cleaned, and broken. Ferrotungsten containing less than 1 per cent carbon can be made in a single smelting operation by careful regulation of the carbon in the charge and the use of an acid slag. The product, however, is less pure and the slag loss is higher. In addition, the metal will contain higher phosphorus and sulphur.

**Uses of Tungsten.**—The main use for tungsten is in the manufacture of steel, especially high-speed steel. Such steel is generally made by the crucible process, although not always. A steel suitable for such use may contain as high as 15 or 20 per cent tungsten, and as low as 8 or 10 per cent tungsten, and 4 per cent chromium. Vanadium and molybdenum may also be used in small quantity,

<sup>1</sup> Bull A I M E (August, 1918), 1338.

and uranium has in some special steels partially replaced the tungsten. Tungsten is also used in self-hardening steels, or those requiring no tempering after forging. They may have a composition between the following limits: W, 2.4 to 3.4 per cent; Cr, up to 6 per cent; C, 0.4 to 2.2 per cent; and Si, 0.2 to 3 per cent.

The chief property which tungsten gives to steels is tensile strength, which, with the elastic limit, increases within certain limits as the percentage of tungsten increases. Elongation and resistance to shock diminish proportionately, and the hardness increases fairly consistently with the per cent of tungsten. Tungsten is also used for filaments in electric lamps. For making the filaments, the "squirting" process was originally employed. This involved mixing metallic tungsten powder with an organic binding material, such as gum, and these were squirted into the filament. The carbon was eliminated by placing the filament in an atmosphere containing a volatile compound of tungsten, such as the oxychloride, and a small quantity of hydrogen. On heating the filament by an electric current, the carbon was replaced by tungsten.

Another method consists in mixing metallic tungsten powder with an amalgam containing equal amounts of cadmium and mercury and squirting the mixture through a die in the usual way. The cadmium and the mercury in the filament are volatilized by heating and the filament retains the usual brittleness, but after continued heating at higher temperatures the filament becomes pliable and can be bent. Drawn filaments are now used, the drawing being made possible by hammering, heating, swaging, etc. Tungsten is also a constituent in the so-called "bronze powders" employed for decorative purposes, and has also been used to a small extent in the fireproofing of cloth and other fabrics, as a mordant for silk, and for coloring glass and porcelain.

**Analytical Methods for Tungsten.**—Tungsten in ores can be determined quantitatively by the following method: The ore ground as finely as possible in an agate mortar is fused with from five to ten times its weight of sodium-potassium carbonates and extracted with hot water. If any gritty particles remain, another fusion is necessary. An equal volume of concentrated hydrochloric acid is added to the aqueous solution of the alkaline tungstate, and the whole evaporated to dryness, after which the silica is dehydrated by heating at 120°C. for an hour. The residue is moistened with hydrochloric acid, taken up with water and boiled; then filtered and washed with 5 per cent HCl or ammonium nitrate solution. The filtrate contains a small amount of tungsten, which is determined by heating the filtrate and the washings to boiling and adding 5 to 6 c.c. of a cinchonine solution, made by dissolving 25 g. of cinchonine in 200 c.c. of 1:1 HCl. This is allowed to digest on a hot plate, while the other operations are being performed.

The precipitated tungstic oxide is dissolved in hot ammonia solution (Watt's solution of 200 c.c. of strong ammonia, 1,000 c.c. of water, 10 c.c. of HCl), filtered into a platinum dish, the filtrate being washed with the ammonia solution and evaporated to dryness and ignited. The cinchonine precipitate is filtered and washed with hot dilute cinchonine solution (100 c.c. water to 5 to 6 c.c. of the above solution), dried, and ignited in the platinum dish with the tungstic oxide. A few drops of sulphuric acid and a little HF are added, and the  $\text{SiO}_2$  driven off at a dull red heat. The tungsten is weighed as  $\text{WO}_3$ . Small quantities of impurities may be removed by treating the  $\text{WO}_3$  with the ammonia solution, filtering, and again igniting.

Ferrotungsten can be analyzed by the following method, which was used at the laboratories of the Tungsten Products Co. at Boulder, Colo.

The refined ferrotungsten, crushed and rolled to pass a  $\frac{1}{2}$ -in. mesh screen, goes to a machine which automatically mixes, samples, and sacks the product for shipment. The sampler is of a type developed by this company, which cuts one-fifth of the total mix. This cut passes through the machine again after being rolled to approximately  $\frac{1}{4}$ -in. mesh. If the original mix is very large the operation is repeated to bring the weight of the sample down to less than 500 lb. This final sample from the automatic is passed repeatedly through a riffle sampler until the last cut weighs 15 to 50 lb. This goes to the laboratory sampling department, where it is reduced in a steel mortar to pass a  $\frac{3}{16}$ -in. screen. The pounding necessary for this process is done by a 2-in. Ingersoll Rand piston drill set up vertically in a frame above the mortar and pestle in such a manner that it is used as an air hammer. The sample is thoroughly mixed and split twice, and one-quarter is then further reduced to pass a 10-mesh screen. This procedure of screening, mixing, and splitting is continued through a series of screens until the last portion passes the 200-mesh screen, giving the analyst about 100 g. of finely powdered metal. The operation of reducing a 20-lb. sample received from the smelter to a 100-g. laboratory pulp of 200-mesh powder by this system requires about 1 hr.

For the determination of tungsten, two 1-g. samples are mixed separately in nickel crucibles with about 5 g. of sodium peroxide and a cover of sodium carbonate. Fusion is done in an electric muffle at about 800°C., which requires 6 to 7 min. to make a perfect decomposition. Cool, leach out in water in covered 400-c.c. beakers. Remove crucibles and acidify carefully with hydrochloric acid, using a moderate excess. Add about 2 c.c. nitric acid or  $\text{H}_2\text{O}_2$  to assist in dissolving any small fragments of nickel oxide scale and bring to a boil. Most of the tungsten separates as  $\text{H}_2\text{WO}_4$  and all iron and nickel salts are in solution. Add about 40 c.c. cinchonine solution, stir and let stand in a warm place for about 4 hr. or preferably overnight. This precipitates all the remaining tungsten as cinchonine tungstate, and it has proved to be just as effective a reagent for this purpose as quinine hydrochloride. Filter off the settled precipitate through a 15-cm. close-weave paper arranged over a platinum cone and suction flask. Wash thoroughly with warm, dilute cinchonine wash water, using gentle suction. No trouble will be experienced due to the precipitate sticking to the beaker if a few drops of hydrofluoric acid are used.

The washed precipitate is transferred to a shallow gold dish of known weight and ignited to  $\text{WO}_3$  in the muffle. Cool, moisten with 10 or 12 drops of hydrofluoric acid to remove any traces of  $\text{SiO}_2$  which might be carried down, dry, and ignite again. Weigh and calculate to W. The factor is 0.793. Duplicate determinations carried out in this way should check to within 0.10 per cent. The proportions used in the cinchonine solution are 50 g. of cinchonine alkaloid dissolved in 2 l. of cold water containing 150 c.c. of hydrochloric acid; for the cinchonine wash water, 100 c.c. of the above cinchonine solution and 50 c.c. of hydrochloric acid diluted to 1 l. with hot water and used from a bulb wash bottle is convenient. For the determination of carbon—ferrotungsten and tungsten metal powder burn completely and readily in oxygen—and carbon is easily determined in any type of combustion train. In the laboratory mentioned they prefer to catch the  $\text{CO}_2$  in a Meyer bulb in 2 per cent barium hydrate solution, to filter, wash, and weigh the  $\text{BaCO}_3$ .

The usual fusion-oxidation methods of determining sulphur are all open to objections when applied to a ferroalloy or other material whose sulphur content is below 0.05 per cent. The blank is always high, due to traces of sulphates in fluxes and reagents used and the danger of picking up fumes or traces of sulphuric acid from the apparatus of a general laboratory. The sulphur content of ferrotungsten occurs as sulphides, which, in a finely ground sample, are completely decomposed, yielding  $\text{H}_2\text{S}$ . This suggests at once the application of the method which has been used successfully for two years. Two to five grams of 200-mesh ferrotungsten or metal powder are

weighed into an evolution flask. Cover with 50 c.c. of water and add 25 c.c. of strong hydrochloric acid by way of the separatory funnel. Heat to boiling and boil for about 10 min., catching the evolved gas, air, and steam in ammoniacal cadmium chloride solution. The usual yellow precipitate of cadmium sulphide shows the presence of sulphides in the alloy. Wash the cadmium chloride solution from the bulbs, then cool, acidify with hydrochloric acid, and titrate at once against a weak iodine solution (1 c.c. = 0.0005 g. of sulphur), using starch as an indicator. The iodine solution is standardized by using a government standard steel of known sulphur content, or by using a ferrotungsten of known sulphur content. Boiling with dilute hydrochloric acid does not dissolve the alloy, but does decompose the sulphides present, as may be shown by filtering off the contents of the evolution flask after the operation and examining for sulphur by a fusion method or by a combustion method.

The removal of phosphorus from the alkaline liquor after a fusion decomposition of ferrotungsten presents certain difficulties. Precipitation with magnesia mixture from dilute solutions is incomplete unless much time is allowed for this step, also precipitation from concentrated solutions either as magnesium-ammonium phosphate or as aluminum phosphate tends to drag down some tungsten, involving another step for its removal. To avoid these difficulties, the use of uranium acetate has been introduced at this stage. The precipitation is quantitative from moderately dilute solutions and no dragging down of tungsten occurs. Weigh a 1-g. sample into a nickel crucible containing 6 to 8 g. of chemically pure  $\text{Na}_2\text{O}_2$ . Mix thoroughly and cover with about 1 g. of chemically pure  $\text{Na}_2\text{CO}_3$ . Ignite in a muffle to complete fusion of the fluxes. Cool and leach out carefully with warm water in a 250-c.c. covered beaker. Remove the crucible and partly neutralize the  $\text{NaOH}$  with 25 c.c. of  $\text{HCl}$  (1-3) to permit filtering without dilution. Stir and then allow the dense  $\text{Fe}(\text{OH})_3$  to settle out while standing on a warm plate. Decant off through a 12½-cm. qualitative paper into a 600-c.c. beaker. Wash the precipitate into the filter, allow it to drain thoroughly, then give it two good washes with hot water, stirring up the precipitate well with a fine jet. Reserve this precipitate of  $\text{Fe}(\text{OH})_3$ , which contains a small amount of phosphorus, to add to the uranium precipitate obtained from the tungsten solution.

Acidify the filtrate of sodium tungstate and sodium phosphate with acetic acid, using 30 c.c. of 40 per cent acetic. Add 2 c.c. of 5 per cent uranium acetate solution. Boil off all  $\text{CO}_2$ . Make just alkaline with  $\text{NH}_4\text{OH}$  (1:1). This will require about 20 c.c. The precipitate is ammonium uranyl phosphate. Add 2 c.c. more uranium acetate, which precipitates at once as uranium hydroxide and serves to drag down the last traces of phosphate, as well as to assist in filtering the ammonium uranyl phosphate. Boil off any large excess of  $\text{NH}_4\text{OH}$ . Filter through a qualitative paper and wash twice with hot water to remove tungsten. Place the precipitate in the same beaker together with the iron precipitate obtained above, add 30 c.c. water and 25 c.c. strong nitric acid. Boil until both precipitates are in solution and the filters reduced to pulp. Filter into a 500-c.c. Erlenmeyer flask, washing the pulp once with hot water. Add 5 c.c. of 5 per cent  $\text{KMnO}_4$  solution to acid filtrate. Boil to oxidize all phosphorus to  $\text{H}_3\text{PO}_4$ . Clear of  $\text{MnO}_2$  by adding 2 c.c. of  $\text{H}_2\text{O}_2$  (1:1). Boil to remove excess  $\text{H}_2\text{O}_2$  and cool under the tap. Add 45 c.c. of  $\text{NH}_4\text{OH}$  (1:1), which will nearly neutralize the nitric acid, then 50 c.c. of molybdate solution. Stopper the flask and shake for 5 min., and let stand at least 15 min. before filtering. Filter through a 9-cm. filter. Wash with acid ammonium sulphate wash solution to remove all nitromolybdate. Dissolve the yellow phosphomolybdate in hot dilute ammonia water, which must be free from chlorides, into the same Erlenmeyer flask. Wash the paper well with alternate washes of ammonia water and hot water. When cool, acidify with 5 c.c. of  $\text{H}_2\text{SO}_4$  (1:1) and pass through the reductor, following with a

thorough wash of cold water. Titrate against standard  $\text{KMnO}_4$  solution to the same end point as used in determining the reductor blank. The iron value of the standard permanganate solution times 0.0163 equals the P value. The ammonium sulphate wash solution must be distinctly acid. A good formula is:  $\text{H}_2\text{SO}_4$  (1:1) 100 c.c.;  $\text{NH}_4\text{OH}$  (1:1) 60 c.c.; water, 21. If convenient, it is well to allow the precipitate of yellow phosphomolybdate to stand about an hour after shaking for 2 min. A blank on all reagents, including a fusion of  $\text{Na}_2\text{O}_2$  and  $\text{Na}_2\text{CO}_3$ , should be carried through with the determinations. It is sometimes desirable to add a measured quantity of dilute phosphate solution of known phosphorus content to the blank for close work. Checks should agree within 0.015 per cent P.

### MOLYBDENUM

(Atomic weight = 96)

**Occurrence.**—The chief commercial minerals of molybdenum are: molybdenite ( $\text{MoS}_2$ ); wulfenite ( $\text{PbMoO}_4$ ); and molybdite ( $\text{Fe}_2\text{O}_3 \cdot 3\text{MoO}_3 \cdot 7\frac{1}{2}\text{H}_2\text{O}$ ). Of lesser importance are ilsemanite (possibly  $(\text{MoO}_3 \cdot \text{SO}_3 \cdot 5\text{H}_2\text{O})$ ); belonesite ( $\text{MgMoO}_4$ ); and powellite ( $\text{CaMoO}_4$ ). The first three are the only ones from which molybdenum is obtained commercially. Molybdenite contains 59.5 per cent molybdenum and 40.05 per cent sulphur. It is a soft, opaque, lead-gray mineral with metallic luster. It frequently occurs in flakes or scales resembling some micas as regards its cleavage. In hardness it ranges from 1 to 1.5, and readily leaves a mark on a paper of a bluish-gray color. Its specific gravity is from 4.7 to 4.8. The mineral is widely distributed throughout the United States, especially in the West, and, whereas it is found in a large number of localities in small quantities, there are also several large deposits which are being worked commercially.

The most important of these is at Climax, Colo., near Leadville. Here a large portion of a mountain is impregnated with the mineral, and, whereas the grade averages less than 1 per cent  $\text{MoS}_2$ , the amount of ore available is very large. Another large deposit is on Red Mountain, near Empire, Colo., about 50 miles due west of Denver. There are two mills at Climax and one at Red Mountain. Smaller deposits of molybdenite are found in several places in the United States, especially in Arizona, New Mexico, Nevada, California, etc. Wulfenite contains theoretically 26.15 per cent of molybdenum and 56.42 per cent of lead. It is a brittle, heavy, semitransparent mineral with resinous luster and is generally of a wax or orange-yellow color, although occasionally it is olive green, yellowish gray, or even brown. Its hardness is 2.75 to 3, and its specific gravity is 6.7 to 7. It crystallizes in the tetragonal system, and the crystals are commonly square and tabular, and are sometimes very thin. Less frequently, they are octahedral or prismatic. Like molybdenite, wulfenite is widely distributed in the western states; probably the largest known deposit is at the Mammoth mine, Mammoth, Ariz., from which a very considerable tonnage of concentrates has already been obtained. It is, however, found in numerous other places in Arizona, Nevada, and to some extent in New and Old Mexico. Molybdite is a hydrous ferric molybdate, lemon yellow to pale yellow in color, and occurs as an earthy powder, usually as incrustations. Molybdite is an alteration product of molybdenite, probably formed by the interaction of molybdic acid and limonite, the molybdic acid being an oxidation product of the molybdenite.

Molybdite, therefore, is frequently found associated with molybdenite, especially where the latter mineral has had a chance to weather. Molybdenum minerals are found in notable quantities in several foreign countries. Molybdenite is found in Queensland, New South Wales, Norway, and Canada. Only during the last 8

years (written 1923) has the United States produced concentrates of molybdenum minerals in commercial quantities. Up to that time practically all of the world's production came from Queensland, New South Wales, and Norway.

**Extraction from the Ores.**—As ferromolybdenum, which is the chief use for molybdenum, can be made directly from molybdenite concentrates, it is not necessary to treat molybdenite chemically unless molybdic oxide or ammonium molybdate are required for chemical purposes. In such a case, the molybdenite may be roasted to oxide, treated with ammonia, which dissolves the molybdic oxide as ammonium molybdate, filtered, and evaporated to dryness, or to crystallization of the ammonium molybdate. On ignition the ammonia is driven off and may be recovered for further use. Doerner<sup>1</sup> gives an oxidizing roast to a mixture of molybdenite and salt. The presence of the sulphur in the charge, together with the oxidizing atmosphere which is maintained during the treatment, results in the liberation of free chlorine in two stages. In the first stage, the sulphur in the charge is converted by the oxidizing roast into sulphur dioxide, and, in the second stage, the sulphur dioxide together with additional oxygen reacts with the chloride to liberate chlorine. This reacts with the molybdenum, forming volatile compounds, either the chlorides, oxychlorides, or mixtures. The chlorides and oxychlorides pass off to a condensing chamber and are decomposed into molybdic oxide and hydrochloric acid by the action of steam or water. In a later patent, chlorine gas is used in place of the salt.

Wulfenite is a more difficult metallurgical problem than molybdenite. This mineral nearly always carries small quantities of vanadinite, and the two cannot be separated mechanically. K'ssock first used a sodium carbonate fusion method in a small blast furnace. The wulfenite, mixed with sodium carbonate and coke, was strongly heated and the lead was obtained as metallic lead, while the molybdenum went into the slag in the form of sodium molybdate. This slag was used directly in the electric furnace for the making of ferromolybdenum, but the excess of sodium carbonate had very decided and deleterious effects on the furnace linings. Holladay<sup>2</sup> prepares a sodium molybdate slag reasonably free from lead and other impurities, then leaches the slag with water, and adds dilute calcium chloride solution in the cold. This precipitates most of the impurities which are still present, while the molybdenum stays in solution. On filtering and boiling and adding excess calcium chloride, the molybdenum is precipitated as calcium molybdate which can be used for the preparation of molybdic oxide, or can be used directly in the making of molybdenum steel. Conditions for the precipitation of calcium molybdate have been studied carefully by Bonardi.<sup>3</sup>

**Concentration Methods.**—Molybdenite can be concentrated readily by flotation methods. An ore carrying less than 1 per cent can be concentrated to a product carrying 60 or even 70 per cent molybdenite. Usually, mixtures of kerosene and pine oil are used, although other oils give satisfactory results on certain ores. Wulfenite can be concentrated by ordinary milling methods, using tables and slimers. The mineral crushes readily, but an ore carrying as little as 0.5 per cent  $\text{MoO}_3$  as wulfenite can be concentrated with a fair recovery. Vanadinite, which is frequently associated with it, cannot be separated to form very

<sup>1</sup> U S patent 1299580

<sup>2</sup> U S patent 1281961

<sup>3</sup> *Chem Met Eng*, Sept 15, 1919

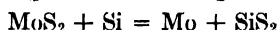
satisfactory products as the specific gravities of the two minerals are almost the same.

**Metallic Molybdenum.**—Metallic molybdenum may be prepared by reducing molybdic oxide with aluminum powder or by heating the trioxide or one of the chlorides in a current of hydrogen. It may also be prepared by heating a mixture of molybdenum trioxide with one-tenth of its weight of sugar charcoal in an electric furnace in a carbon crucible. The pure metal is malleable and is not hard enough to scratch glass. It has a specific gravity of about 9 and can be forged when hot. It oxidizes readily at a dull red heat and is attacked by fused potassium chlorate, nitrate, etc.

**Ferromolybdenum.**—The raw materials for ferromolybdenum may be either molybdenite, molybdic oxide, a sodium-molybdate slag, or calcium molybdate. The reducing agent is usually carbon, although 90 per cent silicon material ground to 60 mesh has been used. Lime and fluorspar are used as fluxes. The reaction that takes place with molybdenite is as follows:



Reduction with silicon metal gives the following reaction:



According to Keeney,<sup>1</sup> for about 100 parts of molybdenite, 58 parts of lime are necessary for slagging the sulphur as calcium sulphide. The reaction works closely to the theoretical, and there is no difficulty in making a product with about 0.1 per cent sulphur and from 1½ to 3 per cent carbon. With sodium molybdate slag, the reaction is as follows:



The reduction of sodium molybdate requires considerably more power than the reduction of the sulphide or oxide. The average power consumption is 7 to 7½ kw.-hr. per pound of molybdenum produced. The recovery varies from 78 to 80 per cent with a loss of 10 per cent in the slag and 10 per cent mechanically by volatilization. Ferromolybdenum containing 80 per cent molybdenum and under 1 per cent carbon cannot be regularly tapped from the electric furnace.

**Uses of Molybdenum.**—The main use of molybdenum is in making molybdenum steel. Undoubtedly, the introduction of molybdenum into steel increases the elastic limit without diminishing its ductility. Molybdenum also may replace tungsten in high-speed steels. Up to recently, only from 0.5 to 2 per cent molybdenum was used, but recently the amount has been considerably increased. High-speed molybdenum steel can be welded with difficulty and is quite brittle on forging. Magnetic steel contains from 2½ to 3 per cent molybdenum and about 1 per cent carbon. A chromium-molybdenum steel has been used recently quite extensively in connection with certain automobile parts, especially where resistance to heavy wear is required, such as in bearings, etc. Such a steel contains 0.2 to 0.6 per cent molybdenum. Ammonium molybdate is used extensively in chemical laboratories. Some salts of molybdenum are also used for coloring glazes in porcelain and to some extent in coloring silks, leather, and rubber.

**Analytical Methods for Molybdenum.**—The following is a revision by Doerner of the method of Bonardi and Barrett of the U. S. Bureau of Mines. Take a

<sup>1</sup> Bull. A. I. M. E. August, 1918, p. 1334

## THE FERROALLOY METALS

0.25- to 5.0-g. sample of finely pulverized ore, add 15 c.c.  $\text{HNO}_3$  and heat until the brown fumes are gone. Carefully add 10 c.c.  $\text{HCl}$  and heat 20 min., or until decomposition is complete. If much lead is present, as in wulfenite, take to fumes with 10 c.c.  $\text{H}_2\text{SO}_4$ , cool, dilute to 60 c.c., and heat to dissolve soluble sulphates. Cool and filter off the lead. Add an excess of ammonia and 5 c.c. of magnesia mixture. If much calcium is present, add 5 g. of  $\text{Na}_2\text{CO}_3$ . Boil 10 min. and filter, washing well with hot water. If the precipitate is large, dissolve it in  $\text{HCl}$  and repeat the precipitation.

In rare cases molybdenite is not dissolved by acids. Fusion with a  $\text{Na}_2\text{O}_2$  and  $\text{Na}_2\text{CO}_3$  mixture is then necessary. The melt is dissolved in water and filtered. The filtrate is saturated with  $\text{H}_2\text{S}$  and barely acidified with  $\text{HCl}$ . Heat to boiling, filter, and wash with hot water. Dissolve the  $\text{MoS}_2$  precipitate in 1 to 1  $\text{HNO}_3$  and take to fumes with 10 c.c. of  $\text{H}_2\text{SO}_4$ . Cool, dilute, filter, and make alkaline with ammonia. The solution should be about 250 c.c. in volume. Make acid with  $\text{HCl}$ , using methyl orange as an indicator, and add 5 c.c. in excess. Add 5 to 10 g. of sodium-ammonium acetate. The addition of 8 drops of  $\text{HNO}_3$  is recommended by Weiser.<sup>1</sup>

Titrate hot with lead acetate solution (about 18 g. of crystallized salt per liter) until a test drop gives no color with a drop of tannic acid solution. For accurate work or to standardize the solution, add 2 c.c. excess of lead acetate, heat 20 min., and filter, washing well with 2 per cent  $\text{NH}_4\text{NO}_3$  solution. Ignite the precipitate and filter in a fire-clay annealing cup in a muffle at dull-red heat. The weight of the  $\text{PbMO}_4$  precipitate times 0.2615 = Mo.

<sup>1</sup> *J. Phys. Chem.*, **20** (1916), 640



## CHAPTER XLI

### METALLURGY OF RADIUM AND URANIUM

BY RICHARD B. MOORE<sup>1</sup>

As uranium is the "mother" of radium, the latter element is always associated with the former in its ores, and ores containing uranium are the only ones which carry radium. Therefore, the metallurgy of these two elements is vitally connected, and must be described in the same chapter.

Since the amount of radium in a radioactive ore is infinitesimal in comparison with the amounts of other metals in their ores, even the less common ones, the methods used are necessarily specialized, and are devised for the treatment of radium ores only. The recognition of this fact has added considerably to the efficiency of radium metallurgy, and has resulted in the ability to handle ores of a grade which could not have been handled in the early stages of the treatment of radium ores. When only 2 or 3 mg. of radium element are contained in a ton of ore, it is obviously necessary to adapt the methods used to the properties of radium and its successful extraction rather than the other elements present. A satisfactory plant control is absolutely necessary in order successfully to treat low-grade ores, and such control is even more necessary when high-grade ores are used, on account of the possibility of the loss of high-grade material.

#### RADIUM ORE DEPOSITS

**Commercial Ores.**—Until recently the two principal commercial ores of radium have been pitchblende and carnotite. The former mineral has no definite composition, consisting of uranium oxides ( $\text{UO}_3, \text{UO}_2$ ) with small quantities of oxides of Pb, Ca, Fe, Bi, Mn, Cu, Si, Al, and rare earths. Carnotite has a more definite composition, being a potassium-uranyl vanadate containing small quantities of barium and calcium. The formula  $\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  expresses its composition fairly well, although not exactly. Of lesser importance are autunite, a hydrated calcium-uranium phosphate ( $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ), and torbernite, a hydrated copper-uranium phosphate ( $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ).

The recent discovery of uranium ores in the Belgian Congo has added to the list of radioactive ores of commercial importance. These include the new minerals curite ( $2\text{PbO} \cdot 5\text{UO}_3 \cdot 4\text{H}_2\text{O}$ ); kasolite ( $3\text{PbO} \cdot 3\text{UO}_3 \cdot 4\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ ); and soddite  $12\text{UO}_3 \cdot 5\text{SiO}_2 \cdot 14\text{H}_2\text{O}$ .

**St. Joachimsthal.**—The pitchblende deposit at St. Joachimsthal, Austria,<sup>2</sup>—is in mica schist interbedded with lime schist and crystalline limestone. Toward the east and northeast the formation is gneiss. The gneiss was intruded by quartz porphyry subsequent to the deposition of the vein material. In the mica

<sup>1</sup> General Manager, the Dorr Co., New York

<sup>2</sup> Beck, Richard, "Lehre von den Erzlagerstätten," 3d ed., vol. 1, pp. 408–410, Borntraeger, Berlin, 1909, "The Nature of Ore Deposits," Translation by W. H. Weed, 1st ed., vol. 1, pp. 254–257 Eng. and Mining Journal, New York and London, 1905

schist are fissures filled with volcanic material which cut the mineralized zone at various points and depths. The veins are usually 6 in. to 2 ft. wide, in rare cases widening out to 3 ft. The mode of mineralization varies greatly, the ores occurring in both stringers and pockets. They contain the following metals: silver, metallic and as argentite, polybasite, tetrahedrite, etc.; nickel, as nickelin, chloanthite, etc.; cobalt as smaltite, bismutosmaltite, etc.; bismuth, as metallic bismuth, bismite, etc.; arsenic, as metallic arsenic and arsenopyrite; and uranium, as pitchblende and other alteration products. Galenite, zinc blende, pyrite, marcasite, and copper occur in minor quantities.

The mines at Joachimsthal have been worked since 1517. In 1545 the production of silver ores declined considerably, but since then the deposits have been mined for bismuth and cobalt. During the last thirty years the mines have been worked for uranium.

*Saxony.*—In the vicinity of Annaberg, on the Saxon side of the Erzgebirge, the silver-cobalt veins resemble those at Joachimsthal. At Johanngeorgenstadt, the veins contain tin and silver-cobalt ores. Where dolomite spar is found, the silver-cobalt ores contain pitchblende, as at Annaberg. In the Gottessengen mine the pitchblende occurs in the spar in pieces 2 to 3 in. in diameter. These mines are worked principally for bismuth ore, but also for cobalt and nickel. In the cobalt-bismuth mines of Schneeberg are found bismutite and various minerals of nickel, silver, and arsenic. There is also some pitchblende, uranochalcite, uranospinite, galenite, zinc blende, etc.

*Cornwall.*—Pitchblende has also been found in Cornwall, England, in the tin region. As at Joachimsthal and Johanngeorgenstadt, the mineral is found associated with nickel-cobalt veins, although only part of the veins are highly argentiferous. Even though these veins are closely connected with the tin veins, they apparently are not of the same age as the latter, but belong to the same general period of mineralization. According to Ussher, Barrow, and MacAllister, "The Geology of the Country Around Bodmin and St Austell," *Memours of the Geological Survey of England and Wales* (1909), page 157, the most important uranium producers were the South Terras mine the Carharrack, Dolcoath, Wheal Unity, Wheal Gorland, Wheal Lowell, and Trenwith. The South Terras mine is situated in the valley of the Fal, southwest of St Austell. The country rock is slate, intruded by greenstone and granite porphyry dikes.

*United States.*—Pitchblende has been found in the following localities in the United States: feldspar quarry, at Middletown, Conn., in large octahedrons; in Hall's quarry, at Glastonbury, Branchville, Conn., in a pegmatite vein and usually embedded in albite; at Marietta, S. C.; in the Baringer Hill District, Llano County, Texas, in the Bald Mountain district, Black Hills, S. D.; in Mitchell County, North Carolina, and in Gilpin County, Colorado. The latter district is the only one of commercial importance.

All of the Gilpin County mines, with one exception, are found on or near Quartz Hill, a few miles from Central City. There are five that have produced pitchblende in quantity the Kirk, Wood, German, Belcher, and Calhoun. The Kirk, Belcher, and German mines are close together on Quartz Hill, the Wood and the Calhoun being in the valley below.

These mines, until recently, have been worked mainly for gold. In this district, gneiss and crystalline schist predominate, with intrusive andesitic dikes and occasionally acid granitic dikes. The rock containing the pitchblende, galena, sphalerite, etc. is a fine-grained aplitic granite which probably once contained an appreciable amount of biotite. The ore deposits are of two general types, one containing pitchblende with pyrite, sphalerite, galena, and sometimes marcasite; the other pyrite, chalcopyrite, sphalerite, and galena, with some gold and silver. Generally speaking,

the two types are not associated, so that the miner has a choice of mining either for pitchblende, or for gold.

The Kirk mine has probably been the most important producer of the five, although reliable data on the output of pitchblende from this mine, up to a few years ago, have been difficult to obtain. During the period 1905-1917, about 20 tons of ore, with an average content of 35 per cent  $U_3O_8$ , and over 100 tons with a content of 3 to 4 per cent  $U_3O_8$ , have been mined. The mine has been shut down for some time. More recent operations of the German and Belcher mines produced 120 tons of low-grade ore, averaging about 1 per cent  $U_3O_8$ , and 6 tons of high grade. Smaller quantities of ore have been produced at various times from these mines and from the Wood and Calhoun, also the Joe Reynolds mine 5 miles west of Idaho Springs, Colo.

**Australia.**—Uranium ores are found in certain localities in Australia. One of these deposits is 80 miles east of Farina, a railroad station on the Great Northern line in South Australia, and lies between Mount Painter and Mount Pitt. H. L. Y. Brown<sup>1</sup> states that the rocks of the district consist of coarse and fine feldspathic, siliceous, and micaceous granite, gneiss, quartzite, and mica schist.

Two of the prospect pits are on outcrops of iron oxide with cellular quartz and gossan, the whole having the appearance of an irregular lode. The uranium minerals, torbernite and autunite, are disseminated through the ore, and are also crystallized on the walls of the fissures and cavities in it. Uranophane and gummite occur sparingly; fergusonite and some monazite are also present. Another uranium deposit lies southeast of the one just described, about 20 miles southeast of Olary, on the railroad line from Petersburg to Broken Hill, South Australia. The ore occurs as a yellow and greenish-yellow incrustation and powder on the faces, joints, and cavities of a lode, which consists of magnetite, titaniferous magnetite, etc., and quartz in association with black mica.

**Portugal**—Autunite is found in commercial quantities in Portugal in the district between the towns of Guarda and Sabugal. An excellent description is given by Segaud and Humery.<sup>2</sup> Apart from the uranium, the rocks of the region are much mineralized, showing deposits of galena, arsenopyrite, chalcopyrite, tungsten, and cassiterite.

**Carnotite Deposits of Colorado and Utah.**—All of the deposits referred to above are important and have been developed as commercial sources of radium; in fact, until about fourteen years ago, they were the only sources from which radium ores were obtained. About 1910, the carnotite deposits of southwestern Colorado and eastern Utah began to receive attention. They were known as far back as 1881, but the composition of the ore was unknown until 1897. In 1899, an analysis showed that the ore not only contained uranium, but was a potassium uranyl vanadate.

In 1900, a small plant was erected in the McIntyre district, south of the Paradox Valley, Colorado, for the extraction and recovery of the uranium oxide from carnotite ore. Only moderate success was achieved, and the plant was shortly shut down. Operations were also started by other concerns, notably the Western Refining Co. and the Dolores Refining Co.; these plants extracted uranium and vanadium only. None of these operations was of importance, and it was not until 1909 to 1910 that any interest was shown in the carnotite deposits as a source of radium. At that time, the ore was almost exclusively shipped abroad.

<sup>1</sup> "Occurrence of Uranium Ore and Other Rare Minerals near Mount Painter, in the Flinders Range of South Australia," South Australia, Mines Dept., 1911.

<sup>2</sup> SEGAUD et HUMERY, "Les Gisements d'Uranium du Portugal," *Ann. mines, Memoires*, Ser. 11 (1913) 3, 111-118.

In the fall of 1912, representatives of the U. S. Bureau of Mines made a thorough survey of the carnotite fields and announced<sup>1</sup> that the carnotite deposits of Colorado and Utah constituted by far the largest known source of radium-bearing ores in the world. Developments since that time have proved this statement to be correct, as the larger part of the radium that has been produced in the world has been derived from American carnotite ore.

The deposits are found mainly in Dolores, San Miguel, and Montrose counties, Colorado, and extend over a belt about 60 miles long by 20 miles wide. The ore is also found to the west of the La Sal Mountains, in Utah, and along the San Rafael Swell, southwest of Green River, Utah. Small patches of ore are found scattered between these points and extend as far north as Meeker, Colo.

The deposits are invariably pockets, many of which, however, are of considerable size. A few individual claims have produced as high as 500 tons of shipping ore, which, however, is exceptional. The ore is found in a light-colored sandstone overlain in places with shale and conglomerate; according to Hillebrand and Ransome, this is the McElmo formation.<sup>2</sup>

*Amount of Radium in Ore.*—Most of the radium obtained at the present time, as has already been stated, is obtained from carnotite ore. The average commercial grade of this ore contains from 5 to 10 mg. of radium element per ton of ore. Some high-grade pitchblende ores may carry as much as 50 to 60 mg. of radium per ton, but this is unusual. Allowing for losses in extraction and recovery, it takes about 5,000 to 6,000 tons of ore to give an ounce of radium element. Therefore, the metallurgical processes involved in the extraction of radium are entirely different from those connected with any other element. Two general steps must be carried out: first, to obtain a radium concentrate from the ore; and, second, the retreatment of this concentrate in order to extract a high-grade product. The first step is necessarily carried out on a large scale, while the major part of the second step is done in the laboratory.

*Belgian Congo.*—Some interesting information concerning the radium ore in Katanga, Belgian Congo, has been given by Mr. Sengier, of the Administrative Council of the Union Minière du Haut Katanga. The discovery of the first uranium mineral in Katanga dates prior to the war. The mineral was first found on Jan. 22, 1913, in the course of prospecting in the Luiswishi mine. Little was done with the discovery at the time, the occurrence of uranium ores being considered of minor interest to the large copper production going on. At that time, also, the demand for radium was extremely small, and no market had yet been developed. In 1920 and 1921, journals in Belgium and other countries published a number of articles concerning the deposits, and this apparently was the first time the world in general knew anything of a possible supply of uranium minerals from the Congo.

In 1914, owing to the war, and to the pressure on the allied governments, the Union Minière concentrated all its efforts on the production of copper, and it was not until after the armistice that the available personnel was returned to the work, and the interrupted researches on uranium minerals were seriously resumed. These researches were accelerated by a second discovery of uranium ore on Apr. 10, 1915, by Mr. Sharp, in another deposit of the Union Minière, called Chinkolobwe (Kasolo) in the course of development work.

The first analysis of this mineral was made in Elizabethville by Mr. Roger, director of the metallurgical work. It was not possible to do anything serious with the deposit until 1921.

On Mar. 31 of that year the company had in its possession the first complete analysis of the ore. The examination and research on the ore were turned over to

<sup>1</sup> MOORE, RICHARD B. and KITHIL, KARL L., "A Preliminary Report on Uranium, Radium and Vanadium," U. S. Bureau of Mines *Bull.* 70, 1913.

<sup>2</sup> HILLEBRAND, W. F. and RANSOME, F. L., "On Carnotite and Associated Vanadiferous Minerals in Western Colorado," U. S. Geol. Survey *Bull.* 262 (1905), 11.

Professor Schoep, of the University of Ghent, who was furnished with samples from Chinkolobwe. This deposit is of vein origin. Its mineralization is related to a tectonic movement, which produced considerable folding, some lateral displacements, and some fractures. One dike was observed in the immediate vicinity of the veins. The course of the veins is extremely irregular and in a direction which follows the dip. Of moderate thickness, they represent a series of small enlargements, diminishing in certain places to mere fractures.

Up to the present time several fragments of veins have been examined without it being possible to define the relation which exists between them. The veins are filled with uranium minerals of varying character. The mineral is separated from the enclosing rock by a small thickness of clay. Where the thickness of the veins is greatest, the primary mineral pitchblende is found in the central part. The exterior part is generally composed of torbernite (a phosphate of copper and uranium). The enclosing rocks are sedimentary, and present the special metamorphism of the copper deposits.

The deposit of Chinkolobwe is situated in a belt containing many outcropping minerals, with copper and cobalt. The varied nature of the deposit, the irregular course presented by the veins, which branch considerably in certain places, and disappear entirely in others, render it difficult to estimate the importance of the discovery by ordinary prospecting methods.

The radioactive minerals of the Congo are considerably different from those found in other countries, such as carnotite in Colorado, autunite in Portugal, and betafite in Madagascar.

In Katanga, the principal ores are related to pitchblende, and the minerals closely allied to pitchblende. Those actually found are pitchblende, torbernite, a uranate of lead, to which the name "curite" has been given, and a silicouranate of lead, which has been called "kasolite." The four minerals are found in the deposit in varying proportions, and with extremely varied uranium oxide content. They are, in comparison with uranium minerals in other countries, exceptionally rich.

The question of whether the mineral should be treated in Africa or in Europe had full consideration, and on account of the high-grade character of the ores, it was found possible to ship the ore to Belgium, the cost of transportation of the raw material being negligible in comparison to the loss of radium that probably would have resulted had the ore been treated in the middle of Africa. The process of treatment was assigned to the General Metallurgical Society of Hoboken, in which the Union Minière has an important interest.

*Madagascar.*—Efforts are being made by the French to develop the deposits in Madagascar in the Ankaratra district. It is reported that 9 tons of uranium oxide were exported two years ago to France, and it is expected that this amount will be increased each year.

Very little detail has been given out concerning the operations in Madagascar, and how extensive the deposits are, but they would appear to be at the present time relatively unimportant.

*Russia.*—The Russian Soviet government has been interested in the Russian radium deposits. One of these deposits is in Siberia, and the other in Turkestan. The minerals are somewhat different from those found in other countries. In Siberia, near Sludjanka, in Transbaikalia, there is an ore which has been called mendelejevit, first described by Professor Vernadsky, which belongs to the betafite group. In Tjaja Mujun (Prialaj Mountains) in Ferghana, Turkestan, the uranium mineral has been called tjujamunit. This was first described by Nenadkevich. The mendelejevit ore does not appear to exist in any appreciable quantity. The Ferghana deposits appear to have greater possibilities for production. The ores here were first described by Professor Antipof and Mr. Karlov. Professor Antipof gave a mineral-

ogical description of them, and described the ore as ferghanite—a uranyl vanadate—containing lithium, which, however, was not afterwards found on further investigation.

During the years 1907–1910, a considerable amount of ore was mined, but no production has been carried on since 1911 by the owners, who are the Ferghana-Metallurgical Company of Petrograd. Previous to the war this company had made contracts with German capitalists, but no ore had been delivered.

Professor Vernadsky believes that the tjujamunit ore is not the most important of those present, but another more complex vanadate of uranium, calcium and copper represents the majority of the deposit. In addition, this ore contains traces of Ba, Sr, Th, As, Bi, and Pb, and it is through the decomposition of this ore that tjujamunit and probably ferghanite are produced. The ore is found in Palaeozoic limestones, and forms irregular nests in connection with old dislocations and faults and the mine is near one of these faults. There are no massive rocks in the neighborhood. The deposit has many similarities to the other localities containing uranyl vanadate, such as Colorado and Utah.

In 1916, all of the radioactive ores produced up to that time were taken over by the Russian government, and the latter began the extraction of radium for military and scientific purposes. The revolution, however, changed all plans, the ores and radium residues being transferred from Petrograd to the Ural Mountains, and from there to Tihija Sody on the Kama, where in 1921 an installation for the extraction of radium was completed. This work is now going on, and the method used is one which has been developed by Prof. V. Chlopiné.

*Canada.*—Some low-grade pitchblende ores have been found in southern Canada in two or three locations. H. V. Ellsworth, who has made a report on these deposits, states that the pegmatites of the province undoubtedly contain in the aggregate a considerable amount of radium and thorium minerals, but these occur in a widely disseminated condition. Low-grade ore containing 1 or 2 lb. of uranium oxide to the ton, he states, might, under certain conditions, prove workable, the tailings constituting a refined ground feldspar product that would be a by-product obtainable probably at a small extra expense. The application of a concentration process would remove not only the radium minerals, but also various impurities, such as magnetite, ilmenite, pyrite, and tourmaline, thus improving the quality of the feldspar. Such a program might be successful after the American carnotite deposits have been worked out, if it were not for the new Belgian deposits in Africa. There is, however, at the present time, no prospect of such a program being carried out successfully.

## METALLURGICAL TREATMENT OF PITCHBLEND

**Metallurgical Treatment.**—Pitchblende was the first ore treated for the extraction of radium. This was done by Madame Curie, who obtained her ore through the Austrian government, from the St. Joachimsthal deposits. The original method was to fuse the ore with sodium sulphate. This converted the uranium into sodium uranate. On washing with water the excess sodium sulphate and other soluble products were separated, leaving the sodium uranate in the residue with most of the other heavy metals, silica, etc. The residue was then treated with dilute sulphuric acid, which dissolved the sodium uranate and some heavy metals, leaving a residue which consisted very largely of silica, alumina, etc. The radium remained in this residue as radium sulphate. The acid solution carrying the uranium was treated for the recovery of this element, while the residue carrying the radium was boiled with a solution of sodium carbonate. This treatment converted a portion of the radium sulphate into

radium carbonate and sodium sulphate. The insoluble product was thoroughly washed free from sodium sulphate, and the residue treated with dilute hydrochloric acid. This dissolved the radium carbonate. The process of the boiling with sodium carbonate was repeated several times until all the radium sulphate was converted into radium carbonate and finally into radium chloride by solution in the hydrochloric acid. The mixed liquors were then added together and a small amount of barium chloride and sodium sulphate added in order to precipitate in the solution a definite amount of barium sulphate. The liquor was kept thoroughly agitated during the precipitation and practically all of the radium was precipitated with the barium sulphate. This product constituted a high-grade radium concentrate, and was refined by methods which will be described later. In many ways still better results can be obtained by fusing the original ore with sodium carbonate instead of with sodium sulphate. After thoroughly washing, the residue, consisting of metallic carbonates and hydroxides, is dissolved in dilute chemically pure hydrochloric acid, and from this a high-grade radium-barium sulphate can be directly precipitated.

If the ore is high grade and largely free from pyrites, it can be treated directly with concentrated sulphuric acid. Radium sulphate is moderately soluble in hot concentrated sulphuric acid, and, on diluting to a concentration of less than 10 per cent free acid, the radium is precipitated as sulphate along with any barium and traces of calcium that may be present. This represents a crude concentrate which can be further refined. The American pitchblende ores cannot be handled in this manner because they contain a considerable amount of pyrites. The pyrite crystals have small particles of pitchblende embedded in them, and, as the pyrite is not soluble in concentrated sulphuric acid, the radium recovery is poor. For the same reason fusion with sodium sulphate or acid sodium sulphate gives also a poor recovery. If a hot sulphuric acid treatment is given, in order to make the process sufficiently cheap, it is necessary to recover the sulphuric acid by reconcentration after the separation of the radium, and this involves some difficulties, as other substances besides radium are dissolved from the ore. The American pitchblende ore is best treated by fusion with sodium carbonate or by the method used by the U. S. Bureau of Mines, namely, boiling the ore with strong nitric acid until all the pyrite is decomposed, diluting, filtering, and then treating the insoluble residue containing the radium with boiling concentrated sulphuric acid in the manner described above.

The method used at the present time by the Austrian government at its plant at St. Joachimsthal is as follows:

The ore as taken from the mine is concentrated and delivered to the radium plant at an average grade of about 50 per cent  $U_3O_8$ . Lots of about 60 lb. of the concentrate are treated separately by grinding the ore, mixing it with sodium carbonate and sodium nitrate, and roasting in small furnaces. During this roasting process, the sulphur and arsenic are oxidized, and the residue is treated with hot water in order to extract the soluble salts. The residue left behind is treated in wooden tanks with dilute sulphuric acid containing a small amount of nitric acid in order to dissolve out the uranium, iron, etc.

The residue from this treatment is boiled with sodium carbonate in order to convert the radium present into a carbonate, and, after thoroughly washing, the radium is dissolved out by treating with c.p. hydrochloric acid in the usual manner, which will be described in greater detail later. Sometimes a caustic soda treatment is given previous to boiling with the sodium carbonate solution in order to eliminate some of the silica.

**Carnotite Treatment.**—The different methods of treating carnotite ore to obtain a concentrate may be classed under four general heads: (1) an alkaline leach followed by an acid leach; (2) fusing the ore with some material that will disintegrate it, and make the extraction of the valuable contents possible; (3) an acid leach; (4) a preliminary treatment followed by sliming which makes a radium concentrate from four to ten times as rich as the original ore.

**Alkaline-leach Methods.**—It is probable that some of the early experimental work on extracting radium from carnotite ore involved boiling the ore with a solution of sodium carbonate, thus getting rid of the uranium and vanadium, which go into solution. Since radium has properties similar to those of barium, any radium in the ore would be converted into radium carbonate, and, on treating the residue with dilute chemically pure hydrochloric acid, the radium would be dissolved with any other acid-soluble products.

The radium concentrate always obtained is radium-barium sulphate. By adding barium chloride and sulphuric acid, or sodium sulphate, to the slightly acid solution carrying the radium, barium sulphate is formed in the solution and drags down radium sulphate with it. The radium is almost always precipitated in this manner in a liquor sufficient in volume to hold it actually in solution. Undoubtedly, adsorption has something to do with the precipitation of the radium along with the barium sulphate, but this does not fully explain the small losses that accompany such precipitation. The term "pseudoisotopy" has been given to this property by Dr. S. C. Lind.<sup>1</sup>

The general principles outlined above are included in the Haynes-Engle process, which involves boiling the ore with an alkaline carbonate solution (U. S. pat. 808,839). The object of this process was to recover uranium and vanadium only, and did not attempt to obtain the radium in any form. A patent taken out by Warren F. Bleeker involved the extra step which the Haynes-Engle process did not cover, namely, the leaching of the residues with hydrochloric acid in order to obtain the radium in solution, after the ore had been boiled with an alkaline-carbonate solution.

The alkaline-leach method has many advantages and some disadvantages. It separates the uranium and vanadium from the ore during the first stage of the process. It eliminates sulphates by converting the metallic sulphates in the ore into metallic carbonates and soluble sulphates, which go into the filtrate with the uranium and vanadium. The radium, therefore, is left behind in the residue as carbonate, practically free from sulphates. This prevents the reprecipitation of the radium as sulphate, on treating with acid, until after the acid solution is filtered from the tailings. On the other hand, it has the following disadvantages: it converts some of the silica in the ore into sodium silicate, which makes filtration very difficult—in fact, most of the filtering and washing has to be done by decantation. It is difficult to treat concentrates by this process, as these are almost invariably of very fine mesh, which adds to the filtration difficulties. The treatment with alkaline carbonate converts much of the iron and a good part of the aluminum in the ore into an acid-soluble form, so that the acid consumption is high. The method, however, can be used with success for the treatment of certain uranium ores, particularly carnotite, autunite, and torbernite.

One firm which uses the alkaline-leach method heats the ore under pressure in an autoclave. This is described in the patent of W. F. Bleeker.<sup>2</sup> It covers the separa-

<sup>1</sup> LIND, S. C., UNDERWOOD, J. E. and WHITEMORE, C. F., "The Solubility of Pure Radium Sulphate," *J. Am. Chem. Soc.* 40 (March, 1918), 465-472.

<sup>2</sup> 1438357, Dec. 12, 1922.



tion of vanadium, radium, uranium, and other compounds from various ores. The process consists, first, of grinding the ore to about 20 mesh, adding 50 per cent its weight of sodium carbonate, and treating the paste so formed in an autoclave at a pressure of about 90 lb. at 150°C. The resulting liquors contain the sulphate obtained by the decomposition of barium and radium sulphate as well as uranium and vanadium compounds. These are at first filtered off and evaporated in some suitable manner. The barium-radium compounds are then dissolved from the residue by means of sulphate-free hydrochloric acid. If caustic soda is added to the sodium carbonate with which the ore is treated, the uranium will remain with the residue and the vanadium only will be dissolved as sodium vanadate. Under such conditions, the uranium would be dissolved with the iron, radium, etc., on treating the residue with hydrochloric acid. R. B. Moore and W. F. Bleeker hold patents covering this treatment.

**Fusion Methods.**—A treatment somewhat similar to the Austrian method for treating pitchblende is given to the ores from Olary, South Australia, by the Radcliffe process. The main uranium mineral is carnotite, but this is associated with considerable quantities of ilsemanite and other rare-earth minerals that are not found in American carnotite. The concentrates are mixed with three times their weight of salt cake, and fused in a reverberatory furnace; the fused product is then crushed and agitated in wooden vats, with water. By suitable adjustments it is possible to separate on the bottom of the vats a considerable amount of comparatively coarse material that is almost free from radium and uranium. The turbid overflow carries in suspension the radium, lead, and barium, as sulphates, together with a considerable amount of finely divided silica. The overflow is pumped to large lead-lined tanks and allowed to stand all night. This is nothing but a sliming process and has the advantage that the radium in the form of sulphate always remains with the fine material. The slimes settle completely in 12 hr. and are collected periodically and treated for the recovery of radium.

The process of Schlundt, which has been used by one company in the United States in connection with carnotite, is very similar to the Radcliffe process. The ore is fused with acid sodium sulphate, leached and washed with water to extract the uranium, vanadium, and other soluble products, and the residue is slimed in order to obtain a crude concentration of the radium, which stays with the fine material.

The U. S. Bureau of Mines has found that if a radium-barium sulphate high in silica is fused with caustic soda containing a small quantity of sodium carbonate, the silica can be easily washed out as sodium silicate, while the barium and radium remain behind as radium-barium carbonates, which can be readily dissolved in hydrochloric acid. Usually the commercial caustic soda contains enough carbonate without the addition of any extra amount. This method has been applied commercially to the treatment of crude concentrates, such as are obtained by the Schlundt process.

One firm at one time used a sodium carbonate fusion. The ore was fused with soda ash, usually about two and one-half times the weight of the ore being required. This was done in a reverberatory furnace, lined with magnesite brick, and the fused mass was run directly into vats, in which it was leached. The silica was thus converted into sodium silicate and so passed into solution, together with the uranium and vanadium. The iron, calcium, barium, radium, etc., remained as the insoluble residue, which was washed in filter presses. The material was then treated with dilute sulphate-free hydrochloric acid, which dissolved the carbonates, and the radium and barium were precipitated by the addition of the requisite amount of sulphuric acid, or sodium sulphate. The whole was allowed to stand in settling tanks and the clear

liquid was drawn off, leaving the barium-radium sulphates mixed with a considerable amount of silica and other impurities, as a sludge at the bottom of the tank. This was taken out without previous filtration, and dried, forming a crude radium-barium sulphate which was then refined.

The main advantages of this method are that it will treat an ore containing considerable quantities of sulphates, as the process removes the sulphates as soluble sodium sulphate in a manner similar to the alkaline-leach method. In addition, it is applicable to the treatment of concentrates, as fineness of material is really an advantage instead of a disadvantage, as it does not involve any "sliming." The main disadvantage is the cost, both for the chemicals and the labor required. The concentrate obtained is also low grade, involving additional refining costs.

**Acid-leach Methods.**—Leaching with hydrochloric acid gives an excellent extraction, provided the ore is comparatively free from sulphates. As a considerable proportion of such ores contain traces of gypsum, it is a method which must be used on selected ores. A hydrochloric acid leach has been used successfully on Cornish pitchblende, which is practically free from pyrite, but is not applicable in any way to American pitchblende, which contains considerable quantities of pyrite. It has also been used on Portuguese autunite and a low-grade sulphide ore from Portugal. In general, the hydrochloric method has a limited use.

Leaching with nitric acid has been used more successfully. This is the method originated by the U. S. Bureau of Mines, and was used in the plant of the National Radium Institute several years ago in Denver, Colo., under a cooperative agreement between the Institute and the Bureau of Mines. As is generally known, barium sulphate is much more soluble in nitric acid than in hydrochloric acid, especially when the nitric acid is concentrated and hot. For this reason, ores containing sulphates can be treated by a nitric acid leach, and the method has been successfully applied to ores carrying as much as 1 per cent of gypsum. On ores carrying small quantities of sulphates the extraction obtained is very high, frequently going, on a commercial scale, to 93 and even to 95 per cent of the radium present. Boiling, 40 per cent nitric acid is used, and filtration is obtained on either a vacuum or a pressure filter. In the early stages of the work, a vacuum filter was used, and this was found to be satisfactory as long as the product treated was not finer than 30 or 40 mesh. Under such conditions the ore could be filtered sufficiently rapidly before the acid cooled to the point where some radium was reprecipitated. Later on, pressure filters were used in order to be able to treat carnotite concentrates, which usually were -150 mesh in size, and even -200. After treating with a hot acid, the whole mass was pumped into the pressure filter, the lid quickly placed in position, and a pressure of about 100 to 120 lb. used. Even on fine material filtration was fairly rapid, but as good an extraction was never made on the concentrates as on the original ore, partly due to the fact that the amount of sulphate in the concentrate was usually higher than in the ore, as traces of gypsum would usually go into the concentrate.

After filtering, the liquor containing the radium, uranium, iron, calcium, etc., dissolved from the ore was run into a large wooden tank and diluted. Caustic soda was then added while the liquor was being stored until a very small permanent precipitate was formed in the solution. This reduced the acidity to a point where the radium-barium sulphate could be precipitated successfully, with a recovery of practically all of the radium. About 2 lb. of barium chloride per ton of ore treated was then added, and sulphuric acid in excess poured into the solution. Agitation was continued for 2 or 3 hr. by means of a revolving stirrer, at the end of which time the liquor, including the precipitate, was pumped into a settling tank, in which it remained for 48 hr. The clear liquor was then siphoned off into a hot solution of sodium carbonate,

there being sufficient excess of carbonate to dissolve the uranium and vanadium and to precipitate the iron and calcium. After filtering, the mother liquor was run into another tank, and caustic soda was added in sufficient quantity to precipitate the uranium as sodium uranate. The filtrate from the sodium uranate was then just neutralized with nitric acid, and ferrous sulphate was added in sufficient quantity to precipitate the vanadium as iron vanadate. The grade of the vanadate can be controlled by the final acidity of the solution. If the solution were faintly alkaline, the iron vanadate would be sometimes under 30 per cent  $V_2O_5$ . If, however, the solution were made faintly acid the grade could sometimes be raised to 42 or 43 per cent  $V_2O_5$ . The sodium uranate usually contains considerable traces of vanadium. This could be removed, however, by sintering with a mixture of salt containing a small amount of powdered charcoal at a temperature of about 800°C. Under these conditions the uranium was converted into  $UO_2$ , and on leaching with water the excess of salt and the vanadium as sodium vanadate were leached out, and the uranium remained as a high-grade oxide.

The filtrate from the iron vanadate contained the acid almost entirely as sodium nitrate with traces of sodium sulphate. The sodium nitrate was obtained by evaporation and crystallization, and was used over again for the manufacture of nitric acid. The average losses of nitric acid were about 15 per cent, so that 85 per cent of the acid used was recovered as sodium nitrate. This actually reduced the cost of the nitric acid below that of hydrochloric, and this, together with the high extraction of the radium obtained, was largely responsible for the low cost of the recovered radium and the success of the method.

The process cannot treat successfully ores carrying as large quantities of gypsum as can be treated by some of the other methods, such as the sodium carbonate fusion, but it is applicable to a large percentage of the carnotite ore produced.

**Sliming Methods.**—Some form of treatment of the ore, followed by sliming, has come into favor recently. The original treatment can consist of either a hydrochloric acid leach, a sulphuric acid leach, or a leach with a mixture of the two acids. A fairly detailed account of such a method has been given by H. D. d'Aguiar.<sup>1</sup> The ore is ground by means of Hardinge or other suitable ball mills to pass 60 mesh, and after careful analysis the ore is sent to the dissolving tanks. These tanks are acidproof and good service is given by tanks constructed of acid-proof brick. The tanks are shallow and about 60 sq. ft. in area. The ore is spread in a layer from 4 to 6 in. deep on the bottom of the tanks, and is then wet down carefully with water or weak vanadium-uranium liquor from previous extractions.

So prepared, the ore is ready for the extraction of the uranium, vanadium, and radium. This is accomplished by treating the ore with the amount of hydrochloric acid necessary to dissolve all values as computed from the chemical analysis, and the number of pounds of ore placed in the tank. During the addition of the hydrochloric acid the ore is continually turned and agitated so that the acid may act evenly on the entire mass. Sulphuric acid is then added in sufficient quantity to precipitate all barium and calcium. Water or more weak vanadium liquor from previous extractions is then added. The stirring is continued throughout the entire operation. The liquor, which now contains the uranium and vanadium in solution and the barium-radium sulphate in suspension, is removed by decantation through an opening in the side of the tank at a height flush with the top of the bed of sand tails. The bed of sand remaining in the tank is washed with water or more weak vanadium liquor, and is again stirred to remove any sulphates. The liquor first decanted and the first wash waters go to a storage tank, while the succeeding wash waters, being weaker in

<sup>1</sup> *Chem Met Eng*, 25, 825.

radium values, go to a second storage tank. These weak liquors are used for first washes on new lots of ore, the sulphates accumulating in this tank being periodically cleaned up and combined with other lots of sulphates.

The sand tails are carefully sampled before being conveyed to the dump and a sample is sent to the electroscopic laboratory for analysis. The tails should show little or no activity. An activity equivalent to 0.05 per cent uranium oxide should be the maximum permissible, the determination being made immediately after drying and cooling.

*Filtering.*—The liquor and the sulphates in the first storage tank are siphoned or pumped to a wooden frame filter press equipped with duriron pumps. The vanadium-uranium liquor passing through as filtrate is pumped to storage tanks. The first wash waters from this operation are also pumped to this tank, while the remaining part of the wash water which shows vanadium is pumped to the storage tanks containing the last washes from the sand tails.

When the press cake has been washed, the press is stripped and the cake sampled and weighed. One portion of the sample is sent to the analytical laboratory for determination of moisture and barium sulphate. The other portion goes to the electroscopic laboratory, where the radium content is determined by means of the emanation electroscopes.

These crude sulphates are transferred to pressure kettles, where water and a calculated excess of sodium carbonate are added, and the mass is "cooked" under steam pressure until the barium sulphate together with the radium sulphate, which always follows barium, is converted to the carbonate with the formation of an equivalent amount of sodium sulphate.

The contents of the pressure kettles are then pumped through iron-frame filter presses. The sodium-sulphate liquor, containing the excess unchanged sodium carbonate, is run to the sewer. However, a careful check is kept on this liquor by sampling frequently and having the samples analyzed to make sure that it contains no radium. A very minute activity is sometimes found, but as a rule these liquors contain no radium.

The frames and cloths used on the filter presses are carefully inspected to make sure that they fit perfectly, and that the cloths are free from thin spots or holes. Any leakage would be the cause of losing radium-bearing material of considerable activity. The radium-barium carbonate so obtained is stripped from the presses, sampled, and weighed. One-half of the sample is sent to the analytical laboratory for the determination of barium and moisture, while the other half goes to the electroscopic laboratory for the determination of radium content by the emanation method.

The barium-radium carbonate so obtained is dissolved in a tank with dilute, sulphate-free hydrochloric acid. This acid chloride solution, together with the insoluble matter, is pumped through a wooden-frame filter press. The filtrate, together with the first wash waters, is run to a storage tank, while the later, weaker, wash water is run to a second storage tank. The press cake, which is chiefly gelatinous silica, requires thorough washing to remove all possible soluble values. This cake is never washed free from radium values, so when the activity has been reduced to the minimum compatible with economical working of the plant, the cake is stripped, and when a sufficient quantity has accumulated the whole lot is reworked separately.

The chloride liquor in the first tank is treated with sulphuric acid to precipitate the barium-radium chloride present as the sulphate. Samples of the liquor are tested from time to time during the precipitation to insure an excess of sulphuric acid.

*Treating with Wash Waters.*—At this time an excess of sulphuric acid is added to the second tank containing the wash waters. The small amounts of

sulphates so precipitated are allowed to settle to the bottom of the tank. The bulk of the supernatant liquor is then decanted through a filter press having wooden frames. When a liquor has been drawn down close to the sulphates, they are stirred up and thus transferred to the press. The sulphates in the main tank are not allowed to settle, but pumping is commenced as soon as sulphation is completed. The filtrate and washings may be discarded. The sulphate cake when washed free from acid is stripped, sampled, and weighed. Barium sulphate and moisture are determined in the analytical laboratory, and the radium content in the electroscopic laboratory by the emanation method.<sup>1</sup>

These second sulphates are transferred to the pressure kettles, mixed with a calculated excess of sodium carbonate, and converted to carbonate by heating with steam under pressure in the same manner as before. When the conversion has been completed, steam is shut off and the carbonates and liquor are pumped through an iron-frame filter press and washed with water until the washings are free from alkali. The washings are tested from time to time by the electroscopic laboratory to make certain that they are free from radium. When the wash water runs free from alkali, the carbonate cake is stripped, sampled, and weighed. The radium content is determined by the electroscopic laboratory, and the barium carbonate and moisture by the analytical laboratory.

If the foregoing operations have been properly conducted, the second carbonates will be of sufficient purity, of high activity, and suitable for delivery to the crystallizing laboratory.

*Recovery of Vanadium and Uranium.*—The vanadium-uranium liquors in the storage tanks, from which the sulphates have been removed, are allowed to collect until the tanks are nearly full. Sodium carbonate is added, until the liquid is but slightly acid, then sodium nitrite is added, and the tank is heated to boiling by steam. If the liquid is but slightly acid at this time, vanadium oxide, carrying some iron and uranium, and considerable amounts of soda salts, will be precipitated. The precipitation is never complete, but if the acidity is checked by volumetric control tests during the process a good recovery is obtained. The precipitate will be granular in character, and will filter readily. When the reaction has been completed, the vanadium oxide is separated by filter pressing. The cake is analyzed for moisture and vanadium oxide. A comparison of the vanadium oxide so precipitated with the amount in the ore treated will give the percentage of recovery. The vanadium oxide so precipitated finds a ready market with manufacturers of ferroalloys.

If it is desired to recover the uranium oxide remaining in the filtrate from the precipitation of the vanadium oxide, it is returned to tanks for the purpose and the uranium precipitated as sodium uranate by addition of sodium hydroxide until the liquor is alkaline. The sodium uranate so precipitated will carry the rest of the iron in the solution, and also the major portion of the unprecipitated vanadium. The precipitate is extremely hard to handle through a filter press, and the lack of a market for any considerable amount of uranium salts makes it nearly always advisable to run the filtrate after precipitation of the vanadium to the sewer without attempting to recover the uranium. Such will be the case, at least, until there is a definite market for the impure sodium uranate.

<sup>1</sup> For the precipitation of the sulphates, a solution of sodium sulphate can be used to good advantage instead of sulphuric acid, provided the price of the sodium sulphate is low enough to make the cost of the sulphate radical contained as low as or lower than the cost of the sulphate radical in the sulphuric acid

The treatment of a crude slime containing radium-barium sulphate, but consisting largely of fine silica and other minerals, is of great importance in the sliming method. It has been found that on boiling such a product with a solution of sodium carbonate in an autoclave, there is a selective action of the carbonate on the radium-barium sulphates present, and practically all of these sulphates can be converted into carbonates without a great deal of action on the other minerals present. This makes the treatment of such slimes practical, as the amount of carbonate required is relatively small. On washing the treated slimes thoroughly with distilled water, and adding sulphate-free hydrochloric acid, the carbonates are dissolved, and a high-grade radium-barium sulphate can be precipitated in this liquor by adding sulphuric acid or sodium sulphate. If the amount of barium in the original ore is very small, it is sometimes of advantage to add a small amount of barium chloride to the ore before receiving its initial acid treatment. This reduces the initial grade of the radium-barium sulphate produced, but reduces losses.

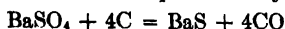
**Refining.**—After the radium-barium sulphate is obtained, it is necessary to change this insoluble product into soluble form so that the radium can be fractionated from the barium.<sup>1</sup> The old method of converting the insoluble sulphates into soluble chlorides consisted in boiling the radium-barium sulphate with a strong solution of soda ash so that the sulphates were converted into carbonates. After the first treatment, the insoluble residue, which consisted of a mixture of sulphates and carbonates, was thoroughly washed so as to free it from soluble sulphates, and was then leached with dilute chemically pure hydrochloric acid. This dissolved out the radium and barium carbonates, which went into solution as chlorides, leaving the insoluble sulphates which had not been converted into carbonates by the first treatment. The process was then repeated; the sulphates being boiled a second time with soda ash, washed, and leached with hydrochloric acid. Three or four treatments usually served to convert all of the sulphates into carbonates, which were ultimately obtained in the form of soluble chlorides by adding hydrochloric acid. All the acid liquors were then added together for fractionation purposes. It can readily be seen that this method involved a considerable amount of time and trouble and added greatly to the cost of radium production.

**Reduction with Coal Gas.**—It is well known that barium sulphate can be reduced by heating in a current of coal gas. A temperature control within reasonably narrow limits is necessary in order to get proper reduction, and at the same time to obtain the material in a non-clinkering condition so that it can be readily removed from the tube in which it is heated. This temperature control is the main objection to this method, as it is difficult to obtain fairly satisfactory results by heating with coal, oil, or gas, and it is not easy to build an electric tube furnace which is suitable for the reduction. With coal gas, reduction begins at about 575°C., the actual working temperature being between 725 and 740°C. The gas consumption averages from 200 to 300 cu. ft. for 25 to 28 lb. of sulphate. The heat of reduction is positive at high temperature, producing reaction clinkers, some of which are friable and some glassy and hard to break. With a high-grade sulphate, reasonably free from silica, the reduction varies from 75 to 90 per cent. If a considerable amount of silica is present, the reduction is decreased. The barium-radium sulphides obtained are dissolved in dilute hydro-

<sup>1</sup> PARSONS, CHARLES L., MOORE, R. B., LIND, S. C., and SCHAEFER, O. C., "Extraction and Recovery of Radium, Uranium, and Vanadium from Carnotite," U. S. Bur. Mines Bull., 104, 1915

chloric acid and the solution filtered from unreduced sulphate. During the reaction with the acid, there is a copious evolution of hydrogen sulphide so that the work must be done outdoors or in a strong draft of air. The solution of barium-radium chlorides thus obtained is ready for fractionation.

A more satisfactory reduction of the sulphates to sulphides can be obtained by using charcoal instead of coal gas. The sulphate is mixed with about one-fifth its weight of powdered charcoal and heated for 7 or 8 hr. in a graphite crucible in an oil furnace at about 800°C. Reduction takes place readily, according to the equation:



The crucible is covered with a lid, but a small opening is left at the spout, at which the carbon monoxide burns. When the evolution of gas is complete, the crucible is allowed to cool with the lid on, and the radium-barium sulphide is removed and broken up. Under such conditions, with a sulphate reasonably free from silica, it is usual to get a 90 per cent reduction of the sulphate to sulphide, the ratio of the reduction of the radium being about the same. The sulphide is then dissolved in dilute hydrochloric acid; the whole is thrown on an earthenware suction filter, and the unreduced sulphate thoroughly washed with distilled water. This unreduced sulphate is either reduced a second time separately, or mixed with a fresh batch of the sulphate. The ratio of radium to barium in the unreduced sulphate is about the same as in the original sulphate, but there is a greater concentration of impurities, such as lead. After these impurities have accumulated, it is more convenient to fuse the final product obtained with sodium carbonate. During this fusion, the lead accumulates at the bottom of the melt as metallic lead, and in this way is eliminated. The carbonates are dissolved in hydrochloric acid.

**Plant Crystallization.**—The liquor obtained from the above procedure will probably carry in solution radium and barium chlorides in a ratio of about 1 part of radium to 1,000,000 of barium. The only efficient method of separation of these two elements so far discovered is fractional crystallization. Radium chloride is less soluble than barium chloride and, therefore, will tend to concentrate in the crystals, whereas the barium will concentrate in the mother liquor.

The crystallization factor in hydrochloric acid solution is about 1.5 to 1.6; that is to say, if 50 per cent of the barium chloride is removed, there will be 50 per cent more radium in the crystals removed than in the liquor left behind.

The crystallization factor in neutral solution is considerably less; therefore, it is advantageous to crystallize in an acid solution. Acidproof ware of some kind must be used; and, as the volumes of liquor obtained from the plant are at first large, it is necessary to have vessels of considerable size. The most satisfactory vessels to use are steel or cast-iron pots with acidproof fused-silica lining. Steam-jacketed vessels of 50 to 80 gal. capacity can be obtained of this material, and, if used carefully, will last a considerable time. The method of crystallization is as follows:

About six evaporators are required. The radium-barium chloride solution in the first evaporator is concentrated so that, on cooling, one-half of the barium chloride crystallizes out. This is richer in radium than the barium chloride in the original solution. The liquor is siphoned into evaporator No. 2, and the process repeated, one-half of the remaining barium chloride being allowed to crystallize. This procedure can be continued all the way down the series, or a fresh batch of liquor may be introduced into the first pot after the crystals have been removed. It is advisable to establish a permanent crystallizing system so that fresh liquor can be introduced each day into evaporator No. 1 and a batch of crystals richer in radium can be taken

out each day for further refining. The system may be established in several ways: either by adding fresh material to the first pot each day and gradually working the mother liquor down the evaporators to the bottom of the series; or by crystallising the first batch of liquor introduced into the first pot all the way down the series before the introduction of fresh material. Whichever method is used, the procedure afterwards adopted is the same. Half of the barium chloride in No. 6 evaporator is crystallized out and removed from the mother liquor. This liquor should be very low in its radium content, carrying not more than 25 or 30 parts of radium per billion of barium. It is discarded. After the crystals have been removed from the evaporator the liquor obtained from a similar crystallization in pot No. 5 is siphoned into No. 6, and the crystals from No. 6 are dissolved in this liquor. In other words, the crystals from each evaporator ascend and the mother liquor at the same time descends, the crystals from a given evaporator being dissolved in the liquor from the second evaporator above. The crystals taken from pot No. 1 can be further concentrated by giving two or three additional crystallizations before being sent to the laboratory for final refining.

**Laboratory Refining.**—The crystals obtained from a plant refining should contain from 5 to 10 parts of radium per million parts of barium. The salts of most metals, such as iron, aluminum, and vanadium, that may occur with the radium-barium salt as impurities, pass into the mother liquors, and only small traces remain with the crystals. Lead is an exception, however, and requires special treatment. Where barium-radium sulphide, after reduction from sulphate, is dissolved in hydrochloric acid solution with copious evolution of hydrogen sulphide, the almost complete removal of the lead content might be expected. This does not occur, however, and some lead always remains with the crystals obtained from the plant crystallization system and must be removed later on. The crude barium-radium chloride received from the plant is dissolved in water in large porcelain dishes, and hydrochloric acid is added to precipitate as much lead as possible. After the solution has stood overnight, it is filtered to remove the lead chloride and whatever carbon and barium sulphate may have escaped previous filtration. All filter papers used must, of course, be retained and afterwards ignited for recovery of the radium retained by the papers. The laboratory crystallizing system is very similar to that used in the plant, except the volumes of the dishes are much smaller and there are at least four vessels on the minus side and whatever number is required on the plus side to bring the refined salt up to the purity desired. If the crystals from the plant contain not more than 5 or 6 parts of radium per million of barium, four crystallizations on the minus side are usually sufficient to reduce the radium low enough so that the tails can be put back into the plant crystallizing system. No. 5 vessel, therefore, counting from the minus end, is the one into which all fresh charges of liquor are placed; and from this point the radium travels up the plus side and becomes more and more concentrated, and the barium travels to the last vessel on the minus side, from which point it goes back with whatever radium it still retains to the plant crystallizing system.

The vessels in which the actual crystallization is carried out may either be of silica, porcelain, or steel, lined with acidproof material. The vessels in which the higher grade material is crystallized should always be of quartz. The procedure is the same as in the plant crystallizing system; for example, the crystals from pot No. 6



are dissolved in pot No. 7 in the mother liquor obtained from pot No. 8. As the factor of enrichment of radium chloride from barium chloride and also of radium bromide from barium bromide is more favorable in acid than in neutral solutions, a fair acid concentration is maintained throughout the chloride and also the bromide system which is afterwards obtained.

**Removal of Lead.**—The chloride crystals from vessel No. 2 on the plus side are dissolved in water without acid, and placed in a large glass precipitating jar 16 or 18 in. high. Make ammoniacal and pass in hydrogen sulphide until the precipitation of lead as lead sulphide is complete. This sulphide is filtered and collected and may be analyzed for its radium content. It should be stored for recovery of the radium by fusion with sodium carbonate. Attempts to precipitate the lead as sulphide even from slightly acid solution usually result in obtaining a brick-red precipitate of the formula  $(\text{PbS})_2 \cdot \text{PbCl}_2$  which is far more soluble in acid than lead sulphide; hence, complete precipitation of the lead is possible only in ammoniacal solution. If the solution is made alkaline with ammonia before passing in the hydrogen sulphide, only a small amount of radium is precipitated with the lead, usually not more than 0.2 per cent.

**Conversion to Bromide.**—Into the filtrate from the lead precipitate, powdered ammonium carbonate is introduced gradually with vigorous stirring until all the barium has been precipitated as carbonate. After standing overnight for the settling of the barium carbonate and the thorough precipitation of the radium carbonate, the supernatant solution is siphoned off as far as possible and the rest is thrown on a Büchner funnel, where it is filtered and washed several times with distilled water. The filtrate which carries only small traces of radium is stored and may be returned to the plant at some convenient point before the precipitation of the radium. The amount of radium in the liquor is surprisingly low, usually 0.001 to 0.003 mg. per liter. The barium-radium carbonate is removed from the Büchner funnel and is dissolved in chemically pure hydrobromic acid of 20 to 35 per cent strength in a large glass precipitating jar.

Fractional crystallization is now continued in silica vessels in fairly strong hydrobromic acid solution in which the separation factor is now 2 instead of  $1\frac{1}{2}$  as is the case for chlorides. Crystallization, therefore, takes place more rapidly, but greater care in handling the vessels is, of course, necessary on account of the higher radium concentration. Heating may be carried on on tripods with bare gas flames until the richer fractions are reached, when the evaporation is carried out on an electrically heated water bath in which only distilled water is used. In case of an accidental loss of radium solution into the bath, all the water can be drawn off and returned into the system just before the treatment with hydrogen sulphide.

The evaporation required to obtain a suitable batch of crystals may be generally regulated by concentrating the solution until vigorous fanning just begins to cause the formation of crystals on the surface of the hot solution. Of course, the higher the acid concentration, the more generous the crystal batch will be, and it is usually convenient to have the acid concentration such that about half of the barium in solution will crystallize out. Owing to the high factor of enrichment as bromide, the radium content of the mother liquor from the "minus two" bromide vessel is extremely low. In general, the amount of radium returned to the plant in this bromide mother liquor is only about 0.2 per cent of the total amount going through the system. If such a result is actually obtained, it is more convenient and economical to use the

bromide mother liquor for the recovery of hydrobromic acid than to return the mother liquor to the plant to recover its small radium content.

**Number of Fractions Employed.**—The number of fractions employed in the plus direction in the bromide system varies with conditions, ten to twelve being the usual number. The crystallization is conducted in such a way that the barium bromide collected in the final fraction should not fall below 1 per cent of radium bromide, and sometimes is as high as 3 or 4 per cent. The total weight of the fraction should be 1 to 2 g. This fraction, after thorough drying in a hot-air oven, is sealed in a glass tube and kept for final purification, when a sufficient number of tubes have been accumulated. The amount of radium in the tube can be easily determined by means of the gamma-ray method, to be described later. After twenty or thirty tubes have accumulated, they are opened and the contents dissolved in hydrobromic acid in a small silica dish.

If there is any considerable difference in the activity of the salt in the different tubes, it is wiser to put those together which have approximately the same activity for the initial solution, and to put those of higher activity in a plus 1, plus 2, or plus 3 dish, depending upon the amount of radium present. Crystallization is then continued with a general tendency to push up the radium from the lower fractions into the last silica dish in which the majority of the radium is finally accumulated. After thorough drying in a hot-air oven to free the salt from moisture and from water of crystallization, it is placed in a glass tube and hermetically sealed. In this tube a small platinum wire is sealed through one end in order to conduct away the unipolar charge that may collect in the interior, attaining voltages that could cause destructive sparking. Reports are on record of serious radium losses having resulted through neglect of this precaution.

## RADIUM MEASUREMENTS

**Measuring Instruments.**—The methods used for determining the amount of radium in either an ore, or in a product such as a concentrate containing radium, depend entirely upon the fact that radium and other radioactive substances ionize gases. Such ionization is due to the alpha, beta, and gamma rays which are emitted by radioactive substances. The methods are, therefore, entirely physical in character and involve any means of recognizing qualitatively or quantitatively the ionization in air or other gases produced by the alpha, beta, and gamma rays. Two instruments are usually employed for such a purpose, namely, an electrometer or an electroscope.

The first instrument is adapted for use in chemical and physical laboratories, and is especially useful where a large number of readings are desired on a radioactive material in a short space of time. For example, where a decay curve is required and the points on the curve involve short intervals of time, an electrometer is very useful, as the length of time for making a reading on even a not very sensitive product is short, due to the sensitiveness of the instrument that may be used. For ordinary practical purposes, however, an electroscope is much more satisfactory, and the use of the electroscope only will be described in detail in this article. A suitable instrument usually consists of two compartments, one above containing a suspended gold or aluminum leaf, in front of which is attached a reading microscope, and one below in which the ore, radioactive solid or radioactive gas, to be tested is placed.

If the material is a solid, there is a suitable door to the lower compartment which can be opened or closed for the introduction of the material. If radioactive gas is to

be tested, the lower compartment is air tight and has two stopcocks, one for exhausting the chamber, and the other for the introduction of the gas after partial or complete exhaustion. Usually the leaf is electrically charged by a piece of vulcanite rubbed on the sleeve of a coat, or by a battery of small dry cells, or any other suitable means of getting a sufficiently high voltage; the charge causes the leaf to rise. Then the natural leak of electricity from the leaf is noted on the scale, using a stop watch to determine the time the leaf drops between two different points, and calculated as a certain number of divisions per minute.

**Approximate Method for Solids.**—If an approximate determination of the activity of a solid such as an ore is desired, the material is placed in the compartment below and the leak of the leaf noted as before. If the ore contains uranium-radium, or any other radioactive element, the rate at which the leaf falls will always be faster than the natural leak of the instrument itself, owing to the ionization of the air in the chamber by the rays given off from the radioactive material. There are a number of precautions, however, to be taken in making such measurements: First, the illumination during the taking of the readings should be constant, and, therefore it is better to have the electroscope in a room artificially illuminated rather than to use ordinary daylight, which will vary from time to time. Second, readings should always be taken between the same points on the scale. Third, in comparing two ores, their physical conditions should be as nearly as possible the same. This may be roughly assured by passing them through the same mesh sieve, preferably 40 or 60 mesh. Of course, every particle of the ore must be ground until it finally passes this sieve. The same weight should be taken and the same surface should be exposed in the electroscope.

In order to get these conditions conveniently, it is advisable to use a brass plate about  $\frac{1}{4}$  in. thick, of a size to fit into the bottom compartment of the electroscope; and in this should be cut, by means of a lathe, a circular depression  $\frac{1}{8}$  in. deep and about 3 in. in diameter. This can be done by any brass worker. The bottom and the sides of the depression should be perfectly smooth. The ore to be tested is poured into the depression, the plate tapped gently so as to settle the ore, and then, by passing the edge of a flat piece of metal across the surface of the plate, the extra ore is wiped off and the depression left exactly filled with ore, having a flat surface. In this manner a fairly uniform weight of material is obtained for comparison, and the surface exposed in the electroscope is approximately constant. Of course, the density of the ores tested varies, but the method gives approximate results. The plate with the ore is introduced into the bottom compartment of the electroscope and a reading taken. The ore is removed and replaced by a sample of carnotite of known uranium content, which serves as a standard. This sample, of course, is passed through the same mesh sieve as the sample being tested. The relative radioactivities, that is, the rates at which the leaf falls, are roughly proportional to the amount of radioactive elements present.

With an ore, the total activity will be due to the uranium, radium, and other disintegration products of the series. With a concentrate, such as radium-barium sulphate, the activity will be due to radium alone. Too much emphasis cannot be placed upon the fact that this method can be used only to compare similar radioactive products, and results are only approximate. For example, a carnotite ore must be checked against an analyzed carnotite ore, pitchblende against an analyzed pitchblende ore, and a concentrate against a similar type concentrate. As has already been pointed out, the physical condition of the material affects the results very markedly.

The following example will show how to make a calculation:

Natural leak of instrument = 5 divisions in 10 min

Natural leak of instrument = 0.5 division per minute.

Rate of fall of leaf with standard ore (3 per cent  $U_3O_8$ ) = 48.5 divisions per minute

Rate of fall of leaf with ore to be tested = 36.5 divisions per minute.

Subtracting from each of these figures the natural leak, 0.5 divisions per minute, the results are 48 and 36. The percentage of  $U_3O_8$  in the ore will then be  $\frac{36 \times 3}{48} = 2.2$ .

If the natural leak is as low as 0.5 division per minute and the radioactivities of the samples are as high as those indicated in the above experiment, the natural leak can be neglected, as the error from it is less than the probable experimental error.

**Exact Determinations by Emanation Method.**—The exact determination of radium is done by means of the emanation method, which involves separating radium emanation as a gas from its parent radium, and measuring its quantity in a gas-tight electroscope previously standardized with a known amount of radium emanation. Analyzed pitchblende has been employed to furnish known quantities of emanation for purpose of standardization. Pitchblende is selected because it is a primary uranium mineral and contains the equilibrium amount of radium to uranium. Therefore, by analyzing the mineral carefully for uranium it is possible to calculate exactly the amount of radium present, and a satisfactory standard is thus readily obtained. Secondary uranium minerals, such as carnotite, autunite, torbernite, etc., do not always contain the equilibrium amount of radium and, therefore, cannot be used as a standard.

Three general methods of procedure may be used, as follows: (1) Release and measure the emanation from a substance in which it is in equilibrium with the radium content. This condition will usually not be fulfilled unless the substance has been retained for a month or more in a closed container. In exceptional instances, however, the radium might be contained in a solid of very compact structure, or with a glazed surface so that no spontaneous loss of emanation could take place. But even with a dense mineral like pitchblende, the leak of emanation, called "emanating power," amounts at ordinary temperature to several per cent.

This circumstance suggests the second procedure: (2) Liberate and measure the emanation retained in the solid and apply as correction the "emanating power," which must be determined separately and preferably after the solid has been in a closed retainer for a month. Both of the above procedures, applicable, in general, to solids only, involve in practice long delays, and, although they are adapted to scientific investigation, they are not suited to radium measurements for the purpose of plant control when quick results are desired.

The following procedure is shorter and preferable when its use is possible; (3) Remove the emanation completely from the sample of the substance to be analyzed for radium, close it at once in a gas-tight vessel and allow the emanation to accumulate for a convenient period, such as from 1 to 10 days. Then remove it and measure it, making a time correction to find the maximum amount that would have been formed on the attainment of equilibrium. For removal of emanation the radium must be contained either in solution, or in a state of fusion. When radium and barium are in a solution together, and there is a tendency for partial precipitation, either as a sulphate or as a silicate, the two elements will usually precipitate in the proportion in which they exist in the solution. The presence, therefore, of a moderate amount of barium in solution has a tendency to hold the radium in solution and to give more exact results by the emanation method.

### **Treatment for Solution Containing Barium in Large Excess over Radium.—**

For a solution containing barium in large excess over radium, the treatment is as follows: Place a suitable portion of the solution—such as will contain about  $1 \times 10^{-8}$  g. of radium—in a small Jena flask and add to it a suitable quantity of 1:1 nitric acid. Add a few glass beads and boil 5 to 10 min. to remove all emanation. Allow slight cooling and then close the flask tightly with a one-hole rubber stopper provided with a glass tube drawn out above to a capillary tip. Seal the tip while some steam is still in the flask, in order to provide a partial vacuum, which should be maintained until the flask is again opened, thus affording a proof that no outward leak of gas has taken place. Note the exact time and date of sealing.

The treatment for a solution containing little or no barium is to add a suitable portion of 1:1 nitric acid which is saturated with barium nitrate, and then proceed as in the treatment described above.

**Procedure for Liquids Containing Excess of Sulphate or Carbonate.—**The detailed procedure for treating a liquid containing an excess of sulphate or carbonate, but no barium, is as follows: An excess of barium salt is added to the liquid, and the precipitate is filtered off. The filtrate containing an excess of barium is made acid with nitric acid to the point of precipitation, and is given the treatment outlined above for a solution containing barium in large excess over radium. The precipitate, if barium sulphate, is fused with four or five times its weight of fusion mixture of sodium and potassium carbonates and is treated as described later for fusions. If the precipitate is barium carbonate, it is dissolved in nitric acid containing sufficient sulphuric acid to precipitate an amount of barium sulphate convenient for fusion, which is filtered off. The filtrate that is obtained may be combined with the original filtrate and given the treatment as described for a solution containing barium in large excess over radium. All radium is then contained either in the filtrate, with an excess of barium, or in the barium sulphate precipitate. The latter is fused with sodium carbonate and treated as described in the next section. Both of the liquid fractions are closed simultaneously (within 15 min.) so that the time of accumulation will be the same for both lots of emanation which can be later introduced into one electroscope to determine the total radium.

**Fusion Method for Radium Determinations.—**If the radium is contained in a substance not readily soluble, such as a radium-barium sulphate, fuse a suitable

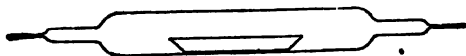


Fig 1 - Apparatus for fusing Ra-Ba sulphate.

quantity in a small platinum or porcelain boat with four to five times the weight of sodium or potassium carbonate and note the exact time at which the material becomes solid. Close this boat in a glass tube as shown in Fig. 1. Allow the emanation to accumulate 2 or 3 days. Connect the glass tube at one end to a highly exhausted electroscope and at the other to a stopcock. Break the glass tips inside the rubber connections and exhaust the air from the glass tube into the electroscope several times, leaving enough vacuum in the electroscope chamber to accommodate the gas to be introduced later. Break the glass tube, remove the boat and its contents, wrap in a filter paper, and place in the neck of a

flask, as shown in Fig. 2; it is then ready for treatment with 1:1 nitric acid after the flask has been connected with the gas burette as shown in Fig. 3. In this treatment the flask is tipped until the acid comes in contact with the carbonate fusion, thus beginning a gas evolution. The stopcock is immediately opened to the gas burette above and the boat and contents are then thoroughly wet with acid and jarred down from the neck of the flask to the body of the acid.

In larger fusions, the evolution of carbon dioxide may become rapid and care should be taken in handling them; but in small fusions not exceeding 1 g. the boat may be shaken down directly into the acid, which should be heated to boiling as soon as the gas evolution begins to slacken. All of the carbon dioxide is, of course, absorbed

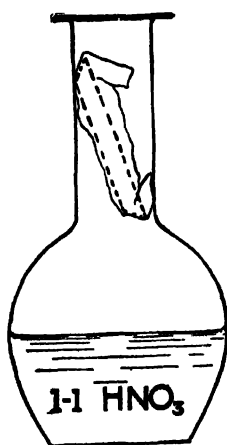


FIG. 2.—Fusion ready for acid treatment.

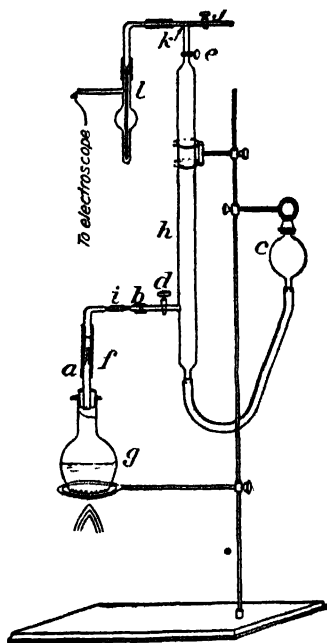


FIG. 3.—Apparatus for evolving emanation and transferring to electroscopes.

by the strong sodium hydroxide solution which is contained in the gas burette. The boiling off from this point is performed as with solutions discussed below.

**Boiling off Emanation from Solutions.**—For boiling off emanation from solutions, the procedure is as follows: Set up an apparatus as shown in Fig. 3, wiring rubber connections at *a* and *b* to insure tightness. Put into the leveling bulb *c* a stick of sodium hydroxide 2 to 3 in. long, or more if a large quantity of carbon dioxide is to be absorbed; make sure that stopcock *d* is closed and stopcock *e* open; pour boiling distilled water into the leveling bulb and allow the alkali to go into solution. If the boiling is too violent, put a one-hole stopper lightly into the mouth of the leveling bulb. After the alkali has gone into solution raise the leveling bulb until the gas burette is filled to the stopcock *e*. If the quantity of air to be boiled off is small, some air may at first be left in the gas burette. Close

stopcock *e* and lower bulb *c* to its original position. Break the glass tip *f* inside the rubber tubing at *a*, and slowly open *d* to ascertain whether there is vacuum in the flask *g*. If so, close *d* again and begin to heat flask *g* over wire gauze. Test the vacuum every few seconds and as soon as the pressure is outward open *d*, and cause the flask to boil vigorously. Continue boiling until live steam has heated to boiling all the liquid in the gas burette *h*. This boiling should never be less than 5 min., and sometimes 10 to 15 min. of boiling is desirable. After the glass tip *f* has been broken, the liquid is likely to be carried upward by steam and in some instances has lodged in the stopcock *d* and caused serious explosions. As a precaution, a roll of thin platinum foil can be introduced into the glass tubing, as indicated at *i*, or the stopcock *d* may have a wide bore, which also obviates the danger mentioned.

After the boiling off has been completed, remove the flame, and as soon as the liquid begins to draw back through the stopcock *d* close the stopcock and remove the flask entirely. Evacuate the electroscope chamber to a suitable vacuum, either by an aspirator, or, more conveniently, by a hand pump, and connect the sulphuric acid microdrying bulb *l* to the electroscope and to the gas burette as indicated in Fig. 3. Be sure that stopcock *j* is closed; open first the cock of the electroscope for a moment and reclose it; then slowly open stopcock *e* to full width and then gradually open the stopcock to the electroscope, allowing the gas to bubble through the microdrying bulb at a fairly rapid rate.

When the liquid in the gas burette has risen exactly to the point *k* close stopcock *e* and open stopcock *j*, allowing dry, dust-free air, which should preferably be taken from outside the laboratory, to sweep out the connections for a few minutes; then close the stopcock to the electroscope, reopen stopcock *e*, and allow the liquid in the gas burette to fall back 3 or 4 in. below the shoulder; close *e*, and then pour off all excess liquid out of *c*; close *j* and again open *e* to the electroscope, allowing air to bubble from the bottom of the gas burette *h* through its entire length to insure the removal of any emanation that may have remained dissolved in the liquid. Air should be allowed to bubble into the electroscope chamber until normal pressure has been almost restored. The above procedure for boiling off radium emanation is used for carbonate fusions introduced into acid, and also in handling any solids that are to be dissolved directly. For example, ground pitchblende and carnotite ore may be wrapped in filter paper in the way in which such a fusion is wrapped in Fig. 3, or sealed in small glass bulbs which are opened by being crushed against the bottom of the flask by tapping on the glass stem projecting through a second hole in the rubber stopper.

**Construction of an Electroscope.**—Figure 4 shows an electroscope which is very suitable for radium determinations by the emanation method. Figure 5 represents a section of this electroscope, showing the gas-tight chamber at the bottom with openings at *o* for connections with stopcock. The electrode *e* is a brass cylinder  $\frac{1}{2}$  in. in diameter. It is suspended by a small brass rod  $\frac{1}{8}$  in. in diameter, which screws into the top of the electrode, passing upward through the insulating material *d*, and terminating in a small conical top *c*, serving to make metallic contact with the leaf system above. The leaf system *f* is supported from the top of the cylinder, where it is held in place by the sealing-wax insulation set in a milled-head cap *g*, which screws into a vertical collar on the cylinder  $\frac{1}{4}$  in. in height. The cap is hollowed out inside to contain the insulating wax, from which a flat brass rod *f*,  $\frac{1}{4}$  in. broad, about  $\frac{1}{16}$  in. thick, and  $2\frac{1}{4}$  in. long, projects downward, terminating below in a light brass spring *s*, to make contact

with the conical top of the electrode of the ionization chamber. The leaf is of aluminum, about 2 in. in length, and is attached to a small offset at the top of the brass rod by a moisture contact. The electroscope can either be charged by a piece of hard rubber or, better, by a battery of flashlight storage cells giving 500 or 600 volts. The reading microscope in front of the instrument carries a micrometer scale serving to measure the rate of discharge of the leaf. The eyepiece fits firmly into the case so that its rotation is difficult after the micrometer scale has been set parallel to the leaf.

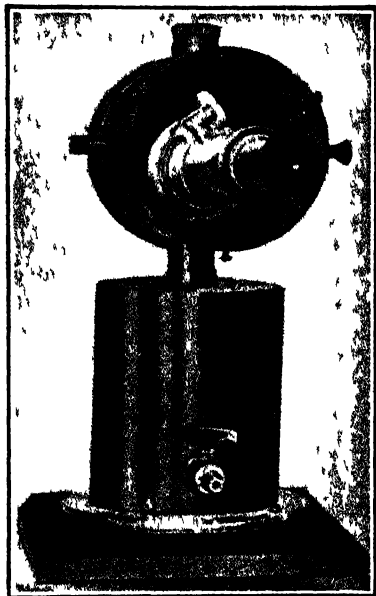


FIG. 4 — Electroscope with interchangeable ionization chamber

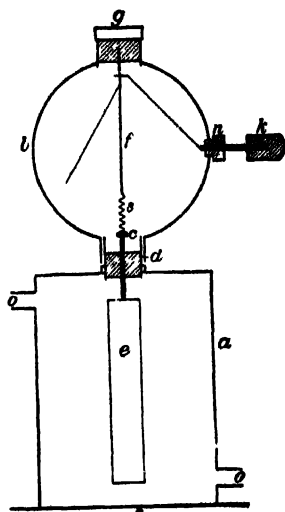


FIG. 5 — Cross-section of electroscope (one-fourth size)

**Order of Procedure in Using Electroscope.**—(1) Set up electroscope and charge for 15 min from a battery with just sufficient voltage to hold the leaf on the part of the scale to be used later. (2) Observe the natural leak during 15 or more min. (3) Carry out the calibration control by means of penetrating rays if radium is available for this purpose. (4) Detach the top and evacuate the lower chamber to the desired vacuum. (5) Pass the emanation-air mixture through a sulphuric acid drying tube into the evacuated chamber and restore normal pressure. (6) Allow the emanation to stand in the discharge chamber for 3 hr. (7) Charge for 15 min as before. (8) Take three readings if agreements are good, or ten if deviations are greater than 1 per cent. (9) Clean out the emanation chamber by drawing dry, dust-free air through it for some time (overnight if convenient). (10) Calculate the discharge and subtract the natural leak, expressing both in divisions per second. (11) Compare the corrected discharge with the calibration of the instrument to determine the quantity of radium under measurement, taking time corrections into consideration.



**Calibration of Electroscope.**—The calibration of the electroscope is carried out in exactly the same way as in ordinary measurements, except that a known quantity of emanation is introduced. This known quantity may be obtained in two ways, as follows: (1) From a standard solution of some radium salt by passing air through it until its emanation is all transferred into the electroscope. This method is not satisfactory, as it is difficult to know always the amount of radium in solution, owing to the tendency of a portion of the radium to precipitate out of solution as sulphate or silicate. (2) The preferable practice is to use high-grade analyzed pitchblende, a suitable quantity being dissolved for each standardization, and the quantity of radium being calculated from the uranium analysis. The quantity of radium emanation obtained on dissolving the pitchblende will not correspond exactly to the radium content because a small fraction of from 2 to 10 per cent of the gas diffuses from the ore; this fraction, termed the "emanating power" of the ore in the cold, must be determined by sealing a quantity of the ore in a tube for a month or more, and drawing off the emanation into an electroscope by the passage of air. The "emanating power" thus determined in the standard sample is used as a subtraction correction. Convenient quantities of radium emanation are those that will produce a discharge of the order of one to two scale divisions per second. The use of pitchblende as a standard is based upon the fact that in any unaltered uranium mineral the ratio of the radium present to the uranium is constant. One gram of uranium is in radioactive equilibrium with  $3.3 \times 10^{-7}$  g. of radium.

**Sample Determination of Radium Content of an Ore.**—A sample of pitchblende loses 10 per cent of its emanation at room temperatures. It contains 50 per cent metallic uranium. Therefore 22 mg. of the ore will, on dissolving in acid, liberate emanation in equilibrium with 10 mg. (0.01 g.) of metallic uranium. This emanation, 3 hr. after introduction into the electroscope, causes the leaf to fall at the rate of 40.5 divisions per minute. The natural leak (0.5 divisions per minute) subtracted from this leaves 40 divisions per minute due to the emanation. Therefore the fall of one division per minute represents the total emanation associated with  $\frac{0.01}{40} = 2.5 \times 10^{-4}$  g. of uranium in the mineral. This is the "constant" for the electroscope. One gram of ore is fused with fusion mixture as already described. At the end of a month the emanation obtained from the two solutions is introduced into the electroscope. After 3 hr. the rate of fall of the leaf is 18.5 divisions per minute. Subtracting the natural leak (0.5) leaves 18 divisions per minute. Therefore 1 g. of the ore contains  $18 \times 2.5 \times 10^{-4} = 45 \times 10^{-4}$  g. of uranium.<sup>1</sup> As 1 g. of uranium is in radioactive equilibrium with  $3.3 \times 10^{-7}$  g. of radium, 1 g. of the mineral will contain  $(45 \times 10^{-4}) \times (3.3 \times 10^{-7}) = 1.48 \times 10^{-9}$  g. of radium.

### OTHER RADIOACTIVE ELEMENTS

**Mesothorium.**—Of the other radioactive elements which have commercial use mesothorium is the most important. It is a disintegration product of tho-

<sup>1</sup> This is true only when the uranium and the radium are in equilibrium. In other cases it represents the theoretical amount of uranium in equilibrium with the radium actually present. In pitchblende, since it is a primary mineral, the ratio of uranium to radium is constant, 1 g. uranium =  $3.3 \times 10^{-7}$  g. of radium, or 2,000 lb.  $U_3O_8$  = 331 mg.  $RaCl_2$ , and if the percentage of uranium is known by analysis, the amount of radium present can be calculated directly. In carnotite and other recent uranium minerals, the equilibrium ratio is not constant and the radium present has to be found by experiment.

rium and is, therefore, associated with this metal in all thorium minerals. Its half-life period is very short, compared to that of radium, being only five and a half years. Therefore, commercially it has not the same value as radium, especially for cancer treatment, or for purposes where it would naturally be carefully preserved and a long life would be of advantage. When its commercial use is likely to last over a limited period, such as in luminous paint for cheap watch dials, electric push buttons, etc., it is just as useful as radium and can be substituted for the latter element in luminous paint for such purposes. Since mesothorium 1 gives off beta rays only, and the alpha rays are the main source of luminosity in paints used for watch dials, etc., it is necessary for the mesothorium 1 after preparation to be allowed to "ripen" for a year or even two years so that the alpha rays, due to the gradual accumulation of radiothorium, can be used. The general effect, therefore, is for the luminosity of such paints gradually to increase for two or three years and then, after coming to a maximum, gradually to decrease. Mesothorium 1 chemically is allied to barium and radium and, therefore, can be precipitated with barium just as radium is. The usual procedure in manufacture is to add 2 or 3 lb. of barium chloride per ton of monazite treated. When the monazite is heated with sulphuric acid in order to extract the thorium and other rare earths, the barium sulphate and mesothorium sulphate are left behind in the residue and can be recovered from the coarse silica, etc., by sliming. The crude concentrates so obtained can be still further purified by fusion with a mixture of caustic soda and sodium carbonate, by which means the silica is converted into sodium silicate and can be washed away from the barium-mesothorium carbonates, or the silica can be eliminated by the use of hydrofluoric acid. The refined sulphate so obtained is purified by the same methods described under the refining and purification of radium.

**Actinium.**—Actinium was discovered by Debierne in the iron group separated from pitchblende, shortly after the discovery of radium and polonium. Actinium itself is probably rayless, but its first product, radioactinium, has a half-life period of 18.8 days. Actinium preparations when first made increase enormously in activity over a period of several months. It is, therefore, comparatively easy to overlook its presence, unless the preparations are kept and their activity tested periodically. Actinium is easily obtained with iron and rare earths by precipitating barium as sulphate in an acid solution; and this accounts for its presence in pitchblende residues. In working these up, the acid solutions, after removal of polonium by means of hydrogen sulphide, are oxidized and precipitated with ammonia, the actinium being precipitated and the radium and barium, of course, remaining in solution. The precipitate may be extracted with dilute hydrofluoric acid, the insoluble part consisting of La, Di, Ce, and Th retaining most of the actinium. The rare-earth element most closely associated with actinium is lanthanum. In the presence of ammonium salts the precipitation of actinium is far from complete, but is it completely precipitated in the presence of manganese from basic solutions.

**Polonium.** (Radium F).—Polonium is one of the short-lived radioelements, having a half life of 140 days and giving off alpha rays only. Its discovery was due to the fact that it is closely allied to bismuth and precipitates with bismuth in the second group. For this reason it is easily separated from radioactive minerals in crude form by digesting radium containing residues of pitchblende

or carnotite ore itself with hydrochloric acid. A part of the polonium is dissolved and may be precipitated with hydrogen sulphide. The polonium may be purified: (1) by fractional precipitation from solutions made very acid with hydrochloric acid, the polonium being enriched in the precipitate; (2) by fractional precipitation of the basic nitrate with water, the precipitate being enriched; (3) by sublimation *in vacuo*, the polonium being more volatile. By immersing a plate of bismuth, silver, copper, etc. in a hydrochloric acid solution, the polonium is practically completely precipitated. The theoretical quantity of polonium in minerals is 1 g. for 14 tons of uranium element, assuming that no radium emanation escapes from the mineral. As such a condition never exists in nature, the actual amount is less than the theoretical.

**Radiolead.** (Radium D.)—There are three kinds of lead: one representing the final disintegration product of the uranium series; one the final disintegration product of the thorium series; and ordinary lead, which so far as is known, does not owe its origin to radioactive changes. The first has an atomic weight of 206, the second 208, and ordinary lead 207. Since radiolead, or radium D, resembles lead perfectly in all of its chemical reactions, in the treatment of uranium minerals it cannot be separated from the lead which is found in such minerals. It is, therefore, obtained in association with this lead when the latter is precipitated during the refining of the radium-barium sulphate. Common commercial lead contains traces of radium D and is more distinctly radioactive than most other metals. For this reason, in making instruments, a very old lead should, if possible, be employed, as in this the radioactive constituents will largely have decayed. Another source of radium D is old radium, in which the radiolead has to a certain extent accumulated. If, however, a sample of this element is required in concentrated form, the best method is to remove the emanation periodically from a radium solution kept in an air-tight vessel and introduce the emanation into a closed vessel. As the emanation decays, the radiolead will be formed and will be deposited on the sides of the vessel. This can then be dissolved by acid and precipitated by ammonia or other lead precipitants, provided a small amount of lead salt is introduced in order to give a precipitate sufficiently large to be handled.

## CHAPTER XLII

### TIN

By R L HALLETT<sup>1</sup>

**Physical Properties.**—Tin is a relatively soft silver-white metal with a brilliant luster. Its atomic weight is 119. It is not very ductile—it is too soft to permit drawing. It is very malleable, and may be rolled into thin sheets, the property which is utilized in the manufacture of tin foil. The tensile strength of tin is low, being somewhat higher than that of lead but lower than most of the other metals. Most impurities tend to increase the tensile strength of tin, but they also decrease its malleability and ductility.

The specific gravity of tin varies with the method of preparation, the specific gravity of cast tin is about 7.28, of rolled or extruded tin, about 7.30. The melting point of tin is 232°C., and the boiling point has been reported to be about 2200°C.

Most of the impurities usually found in tin tend to make it harder and more brittle. Many of them tend to increase its melting point, but some of them (such as lead) form eutectic mixtures with tin and decrease its melting point.

When tin is exposed to low temperatures, the physical character of the metal seems to undergo a complete change, probably a molecular change, during which the solid metallic form is changed to a gray powder made up of small grains. This form is known as the "gray modification," and seems to be an allotropic modification of tin. The change may take place at temperatures below 18°C. The specific gravity of the gray modification has been reported to be about 5.8.

Tin in its ordinary form is somewhat crystalline in structure, the cast form being more crystalline than the rolled form. When a bar of tin is bent it gives a characteristic "cry," a slight cracking noise, probably caused by the friction of the crystals on each other.

**Chemical Properties.**—At ordinary temperatures metallic tin is not readily acted on by many chemical substances. The action of the elements of the atmosphere is slight, accounting for the wide use of tin as a protective coating for iron and steel in the well-known form of tin plate.

Cold dilute hydrochloric acid dissolves tin slowly,<sup>2</sup> and the action is more rapid when hot concentrated acid is used. Stannous chloride is produced, and hydrogen is given off in the reaction.

Dilute sulphuric acid slowly dissolves tin, with the evolution of hydrogen, and hot concentrated sulphuric acid dissolves tin rapidly, with the evolution of sulphurous anhydride and the separation of sulphur.

Very dilute nitric acid dissolves tin without the evolution of gas, forming stannous nitrate and ammonium nitrate, and strong nitric acid rapidly converts it into meta-

<sup>1</sup> National Lead Co., Research Laboratories. Consultant for Williams Harvey Corporation, New York and Williams, Harvey & Co. Ltd., Liverpool.

<sup>2</sup> Throughout this chapter, reference numbers are to corresponding numbers in Bibliography at the end of this chapter.

stannic acid, which is insoluble in most other acids. *Aqua regia* (nitrohydrochloric acid) dissolves tin readily, forming stannic chloride.

Tin usually acts as a base, but sometimes as an acid. Tin oxide ( $\text{SnO}_2$ ) is not appreciably attacked by most acids, but at high temperatures tin oxide reacts readily with silica to form tin silicates. When tin oxide is heated with some strongly basic substances, such as the fixed alkalies, stannates of the bases are formed.

**Alloys.**—Tin readily forms alloys with most of the other metals. Some of the alloys are of great commercial and industrial value, and the use of tin in alloys is second in importance only to its use as tin plate.

Perhaps the most important alloys of tin are those with antimony and copper in bearing metals, with lead in solder, with lead and antimony in type metal, with lead interne plate, with copper and sometimes zinc in bronze, and many other alloys used for minor purposes.



FIG. 1.—Open cut tin mines, Straits Settlements.<sup>1</sup>

The only tin alloys which greatly affect the metallurgy of tin are the alloys with iron. Tin alloys readily with iron, which fact is said to account largely for the success in plating iron with tin.

The tin-iron alloys formed in some tin metallurgical operations are known as "hard head." They have very high-melting points and introduce certain difficulties in the metallurgy of tin. The best-known hard-head alloy is  $\text{FeSn}_2$ . The alloy containing 50 per cent of tin and 50 per cent of iron has the lowest melting point, which is given at  $1140^\circ\text{C}$ .

**Tin Ores.**—By far the most important ore of tin is the mineral cassiterite, which is tin dioxide ( $\text{SnO}_2$ ). It contains 78.6 per cent of tin and 21.4 per cent of oxygen. It crystallizes in the tetragonal system and has a hardness of from 6 to 7. The specific gravity is from 6.8 to 7.1. The color is brown or black, sometimes red, gray, white, or yellow.

<sup>1</sup> Figs. 1-5 included are by courtesy Malay States Information Agency.

The occurrence of tin as the mineral stannite, a triple sulphide of tin, copper, and iron, has been reported and is of interest, but no deposits of commercial value have been found.

A number of other tin minerals have been identified in various places, but are of scientific interest only.

Tin oxide (cassiterite) is the commercial ore from which the tin of commerce is produced. It occurs in many parts of the world in original deposits in the form of veins or lodes, and also in transported alluvial or placer deposits. The occurrence in these two forms gives rise to the two names for the ore "vein tin" and "stream tin," designating the vein and the placer deposits.

Tin ores are also referred to as "tin stone," "washed tin," "tin sand," "black tin," and "barilla," the different terms being used in different localities where the nomenclature has probably been developed locally.



Fig. 2—Open cut mine, Straits Settlements •

Minerals containing other metals are often found associated with cassiterite in the original vein deposits, but in the placer deposits the tin ores are usually fairly pure, because, while cassiterite is practically unaffected by the action of the elements of nature which decompose the original vein formations and transport the decomposed material to the placer deposits, many of the other minerals are altered to such an extent that the metals contained in them are readily dissolved or washed away and are not found associated with the cassiterite in the placer beds.

The metals often found associated with cassiterite in vein deposits are Pb, Bi, W, Sb, Zn, Cu, Ag, As, and Fe. While the tin almost invariably occurs as the oxide, the other metals when present are nearly always in the form of sulphides, except arsenic and tungsten, which usually occur in the form of arsenides and tungstates.

**Occurrence.**—Tin has been found in many parts of the world, but in some large areas (such as practically the whole of North America) no tin deposits of any great commercial value have been discovered up to the present time.

The large and valuable tin deposits of the world are found in the Straits Settlements (comprising the Malay Peninsula and Burma), Bolivia, the Dutch East Indies, Siam, China, Nigeria, Australia, South Africa, and England, with minor deposits in Portugal, Spain, India, Germany, Mexico, Alaska, and the United States.

The tin ore produced in the Straits Settlements, Dutch East Indies, Siam, and Nigeria is nearly all from placer deposits. The ore deposits which are being operated in Australia are of both placer and vein formation, the production being divided about equally between the two. The commercial ore deposits of Bolivia and China are



FIG 3—Hydraulic mining, Straits Settlements .

nearly all vein deposits, and those of South Africa consist largely of vein deposits. In Cornwall the tin ore was originally recovered from placer ground, but at the present time practically all the commercial tin-ore deposits of Cornwall are of vein formation.



FIG 4—Hydraulic mining, Straits Settlements .

Up to and including the eighteenth century, civilization secured its tin supply mainly from Cornwall in England and from Saxony and Bohemia in Europe. Early in the nineteenth century the European deposits became practically exhausted, but the Cornwall deposits increased in production and importance, and, together with the

## TIN

placer deposits of the Dutch East Indies, formed the main supply until production from the Straits Settlements began to come in toward the end of the nineteenth century and the early part of the twentieth century. At the present time the Cornwall deposits have become greatly depleted and are nearly exhausted. During the first twenty years of the twentieth century the Straits Settlements became the largest producers of tin and have occupied that position continuously until the present time. The production of tin from Bolivia began to be a material factor toward the end of the nineteenth century, and at the present time is second only to the production of the Straits Settlements.

Apparently, the Straits Settlements have passed the peak of their production and will continue to show a decrease in the future. The Bolivian production has been increasing, but, apparently, has about reached its peak at the present time. With the decrease in the production from the Straits Settlements, the indications are that before very long the Bolivian tin deposits will be the most important in the world, and Bolivia will probably be the leading producer. The production from the different localities during the last eight years, as given in "Metal Statistics," is as follows:

Much of the tin ore from the Straits Settlements is smelted in Singapore and Penang, and much of the tin ore mined in the Dutch East Indies (the islands of Banca and Singkep) is smelted locally. Practically no tin ore of the Far East has been smelted in the United States because of the restrictions which have prevented the development of an American tin-smelting industry with the ores from that source. The regulations of the British Empire require that all tin ore produced in Great Britain or her possessions shall be smelted within the British Empire, and similar restrictions in the Dutch East Indies have resulted in local smelting in that locality also. The restrictions in regard to tin ore produced in the British Empire resulted in the virtual control by Great Britain of the tin-smelting industry of the world, up to the time of the development of the Bolivian tin deposits.

Before the World War a large proportion of the Bolivian tin ore was smelted in Germany and the remainder in England. As the war progressed, Germany was eliminated because of her inability to secure Bolivian tin ore, and for several years the tin ore from Bolivia was smelted almost entirely in England and in the United States, each country receiving about half of the Bolivian output.



The tin-smelting industry in the United States was not started until 1916, but rapidly developed thereafter until in 1923 it had reached an annual tin-smelting capacity of about 20,000 tons of fine tin. During 1923 the tin-smelting companies in the United States were forced to abandon their operations, owing to their inability to meet the cheaper costs of smelting tin ore in Europe, chiefly in England and Germany. This condition will doubtless continue unless the industry should be protected by a duty on pig tin imported into this country, without any duty being imposed on the tin contents of ores.

Prior to 1916 the only tin produced by smelters in the United States was the secondary metal obtained from the smelting of dross, scrap, and refuse. Smelting of dross and the recovery of secondary metal still is and will continue to be an important industry in the United States, and the amount of tin so produced is probably about 30 per cent of the primary tin used in the United States.

**Consumption.**—The world's production of primary tin is about 120,000 long tons, of which about half is consumed in the United States. Of the tin consumed in the United States about 40 per cent is used for tin andterne plate, an equal amount for bearing metals and solder, and the remainder in various industries where tin in different forms is required. The United States, therefore, occupies the unique position of being the country which is the largest consumer of tin, but which, aside from the insignificant quantity coming from Alaska, produces no tin from natural deposits and, since the suspension of the tin-smelting industry in the United States, must depend entirely on supplies from foreign countries.<sup>2</sup>

**Grades of Tin.**—With tin, perhaps more than with any other metal, the location and the character of the ore deposits from which the tin is obtained determine to a large extent the value and the use of the tin which is produced. In metallurgical recovery operations most metals are so completely refined that they are eventually recovered in pure form suitable for the purposes for which such metals are used. The methods of refining are usually such that the ores from all sources are amenable to the methods, and pure metals are produced, no matter what impurities may be associated with the metals in the original ore deposits.

With tin, the conditions are quite different, as the selection of tin for various uses depends greatly on the impurities which the refined tin contains, and, because of the difficulty of removing the metallic impurities in the tin-refining process, the success in refining depends to a very large extent on the purity of the original tin deposits and the kind and amount of other metals associated with the tin in the original ore deposits.

For this reason tin from certain localities has become famous not because the metallurgical methods of recovery and refining of the tin in those localities are superior, but because the tin ores produced in those localities contain such small amounts of associated metal impurities that fairly simple metallurgical methods produce refined tin of great purity.

Tin from other sources where the ores are contaminated by large amounts of other metals is refined with great difficulty, and even after refining is usually not so pure as the tin from the localities where the ore does not contain the impurities in the original ore deposits. This condition has developed the present tin situation, where reputation of brand, resulting largely from purity of the original ore deposits, is the first consideration in purchasing the metal.

The metallurgical methods used in different parts of the world have been specially developed to treat the different kinds of ore obtained in those localities, and, for that reason, great differences in metallurgical processes and methods of treatment have resulted.

The metallurgical methods have been carried on for such a long time that they have become more or less standardized in the various localities, and the different brands of tin are fairly uniform in regard to the kind and amount of impurities which they contain. Tin comes from ore deposits located in many parts of the world, and tin from the different deposits varies considerably in purity. The uses of tin likewise vary, as some uses seem to require tin of great purity, while others are satisfactorily met with tin which is somewhat less pure.

The kind as well as the amount of impurities contained in tin is an important consideration. While there are undoubtedly characteristic differences in the composition of tin produced from the different localities, taken altogether, the differences are not great when refining has been properly done. For many years tin has been marketed under the brand or trade name of the producers, which has led to the distinct classification according to brand, and each brand has assumed its own relative importance in accordance with its reputation for uniformity and the kind and amount of impurities which it contains.

The principal brands of pig tin produced by the tin smelters of the world, together with typical average analyses of each brand, as published by the London Metal Exchange, are given in the following table.

TYPICAL TIN ANALYSES

	Tin	Antimony	Arsenic	Lead	Bismuth	Copper	Iron	Silver	Sulphur	Cobalt
American electrolytic tin	99.928	0.002	0.002	Nil	0.042	0.026	Trace			
Banca tin	99.950	0.007	Nil	Trace	Nil	0.018	0.045	Nil	Trace	
Penang tin	99.949	Trace	0.013	Trace	Nil	0.016	0.028	Nil	0.004	
Singapore tin	99.870	0.008	0.045	0.034	0.003	0.052	0.003	0.006	0.005	
Mt. Buschoff <sup>1</sup>	99.795	0.015	0.063	0.037	0.005	0.035	0.042	Trace	0.008	
Pymont tin	99.918	0.017	0.019	Trace	Nil	0.022	Trace	Nil	0.004	
Irvine Bank	99.580	0.082	0.034	0.221	0.025	0.126	0.002	0.018	0.004	
Mellancar Lamb & Flag	99.19	0.16	0.06	0.16	0.35	0.06	0.02			
Williams Harvey & Co. Ltd.										
No. 1	99.800	0.015	0.040	0.004	0.005	0.047	0.003	Nil	0.006	
No. 2	99.560	0.166	0.037	0.162	0.007	0.050	0.005	Trace	0.013	
No. 2a	99.350	0.245	0.065	0.223	0.015	0.042	0.016	Trace	0.013	
No. 3	99.200	0.300	0.037	0.396	0.007	0.100	0.013	0.014	0.006	
No. 4	99.941	0.011	0.022	Trace	0.001	0.020	Trace	Trace	0.005	
Penpoll										
No. 1	99.720	0.118	0.054	0.041	0.007	0.032	0.004	0.009	0.007	
No. 2	98.710	0.569	0.042	0.546	0.055	0.103	0.007	0.015	0.004	
No. 3	99.300	0.325	0.056	0.212	0.050	0.088	0.002	0.021	0.009	
Redruth	99.160	0.176	0.053	0.177	0.017	0.445	0.041	0.006	0.008	0.012
Sutton, T. & Sons	99.550	Trace	0.022	0.342	0.015	0.045	0.010	Trace	Nil	Trace
Chinese No. 1	99.343	0.031	0.040	0.434	0.007	0.052	0.010	Trace	0.011	0.072
Wing, Hong & Co.										
No. 2	98.662	0.039	0.035	1.035	0.012	0.134	0.014	Trace	0.011	0.058
No. 3	95.280	0.381	0.050	3.995	0.020	0.106	0.026	0.018	0.008	0.116
<sup>1</sup> The company's directors issue the following analyses:	99.947	0.015	0.013	0.042	0.001	0.017	0.063			
	99.99			0.05	0.01	0.006	0.01	0.005	0.005	0.04

The location of the smelters producing these brands and the principal sources from which the tin ores are obtained are as follows:

LOCATION OF SMELTERS	SOURCE OF ORES
United States (closed in 1923):	
American electrolytic tin.....	Bolivia
Mellaneer, Lamb & Flag.....	Bolivia
England:	
Mellaneer, Lamb & Flag.....	Bolivia
Williams, Harvey & Co., Ltd.:	
No. 1.....	Bolivia—Nigeria
No. 2.....	Bolivia—Nigeria
No. 2a.....	Bolivia—Nigeria
No. 3.....	Bolivia—Nigeria
No. 4.....	Bolivia—Nigeria
Penpoll:	
No. 1.....	Cornwall—Bolivia
No. 2.....	Cornwall—Bolivia
No. 3.....	Cornwall—Bolivia
Redruth.....	Cornwall—Bolivia (mostly Cornwall)
Sutton, T. & Sons.....	Cornwall—Bolivia
Straits Settlements:	
Penang tin.....	Straits Settlements— Billiton
Singapore tin.....	Straits Settlements
Dutch East Indies:	
Banca tin ..	Dutch East Indies
Australia:	
Mt. Bischoff.....	Australia
Pymont tin..	Australia
Irvine Bank.....	Australia
China:	
Chinese No. 1.....	China
Wing, Hong & Co.:	
No. 2....	China
No. 3.....	China

Williams, Harvey & Co., Ltd., No. 1 tin is known in the United States as "English Refined," and is guaranteed to contain not less than 99.75 per cent of tin. Mellaneer, Lamb & Flag is guaranteed to contain not less than 99 per cent of tin and is known in the United States as "99 per cent." Penang and Singapore brands are known as "Straits tin." Chinese No. 1 tin, accompanied by Hong Kong analysis, is known as "Standard Chinese, Hong Kong Analysis."

**Prices.**—Under normal conditions, where the prices are controlled by supply and demand, the principal markets are in London and New York, and prices are established at those points. Prices in London and New York are usually fairly near together, the London price being just enough under the New York price to represent approximately the cost of freight from London to New York. The average yearly prices of Straits tin for prompt delivery in New York are given in the following table:

FIG TIN PRICES IN NEW YORK

YEAR	AVERAGE CENTS PER POUND
1914.....	35.70
1915.....	38.66
1916.....	43.48
1917.....	61.65
1918.....	86.80
1919.....	65.54
1920.....	50.36
1921.....	30.00
1922.....	32.58
1923.....	42.71
1924.....	50.20
Average for 30 years.....	36.61

**Mining.**—The mining methods used to remove the tin ore from the natural deposits depend to a large extent on the character of the deposits, whether vein or placer, and, to a lesser extent, on the location, kind of labor available, climate, and other local conditions.

The vein deposits are worked by mining methods very similar to those used for the hard-rock mining of the ores of other metals.

The placer deposits are mined with open cuts and by hydraulic sluicing and dredging. Some of the open-cut mining in the Far East is done in a crude and elementary manner, but much of the hydraulic sluicing and dredging is carried on according to the best modern mining methods.

The sand and gravel from the open-cut mines are usually treated in sluice boxes or hand pans to concentrate the cassiterite and wash out the worthless material. Typical open-cut mines in the Straits Settlements are shown in Fig. 1 and Fig. 2.

Where hydraulic sluicing methods are used the placer ground is often broken up with modern "giants" or "monitors," and the sand and the gravel are washed through sluice boxes to concentrate the tin mineral. Hydraulic mining in the Straits Settlements is shown in Fig. 3 and Fig. 4.

Dredging is done with floating boat dredges following practice similar to the dredging of placer ground in other parts of the world.

The tin ore from vein-mining operations is crushed to break the cassiterite away from the associated minerals, and it is sometimes necessary to crush some of the gravel from placer ground to accomplish the same end.

The mined and crushed ore is first treated in sluice boxes, hand pans, or, in the more modern operations, with standard wet-concentrating machinery. As the specific gravity of most of the gangue minerals is lower than the specific gravity of cassiterite, the mechanical concentrating treatment removes most of the gangue, earth, and silicates, and leaves the tin in the form of cassiterite concentrates, usually containing more than 60 per cent of tin. Hand picking sometimes precedes the wet-concentration treatment. In the purchase of tin concentrates by the English tin smelters, the treatment charge is usually based on concentrates containing 60 per cent of tin with an increased treatment charge if the concentrates contain less than 60 per cent of tin, and a decreased charge if they contain more than 60 per cent of tin.

If the ore is obtained from placer ground, the tin concentrates resulting from the mechanical treatment are usually fairly pure, but if the ore is obtained from vein deposits the concentrates may be contaminated with small amounts of the sulphides of other metals.

**Preparing the Ore for Smelting.**—Modern smelting methods, as applied to the metallurgy of tin, are fairly efficient and economical, but, because of the metallurgical and chemical characteristics of tin, the refining methods in general use are not satisfactory and fail to remove completely the metallic impurities which are reduced with the tin in the smelting process. For this reason it is often necessary to treat specially the tin concentrates from some localities so as to remove the metal impurities which they contain and make them suitable for smelting. Tin concentrates from other localities, where the original ore deposits do not contain the metal impurities, require much less treatment to prepare them for smelting, and some tin ores are successfully smelted after simple mechanical concentration to remove the gangue.

Generally speaking, the tin concentrates from vein deposits, particularly those of Bolivia, require the most extensive preparation before smelting, and the tin concentrates from placer deposits require the least preparation.

A number of methods are used to remove the metal impurities from the tin concentrates before smelting, and these methods might be somewhat broadly classified as follows: (1) roasting, followed by further mechanical separation of minerals which are broken away from the cassiterite by roasting, or are altered in such a way as to change their specific gravity and make them more amenable to mechanical-concentrating methods; (2) roasting, followed by leaching with water or with acid solution—dilute solutions of sulphuric acid and hydrochloric acid are sometimes used in this process; (3) heating with sodium carbonate or salt cake (sodium sulphate) followed by leaching with water; (4) chloridizing roast with sodium chloride (salt), followed by leaching with water or hydrochloric acid; (5) the removal of metal impurities, present in the form of sulphides, by oil flotation.

**Roasting Followed by Mechanical Concentration.**—Cassiterite is not decomposed or appreciably altered when calcined at a red heat, but many of the associated minerals containing other metals are so altered as to make further mechanical separation possible. During the roasting process, much of the sulphur and arsenic and some of the antimony are volatilized and removed. After roasting is completed, the resulting material contains tin oxide, substantially in its original form; oxides of iron, zinc, bismuth, and copper; sulphate of lead; some arsenate of iron; and small quantities of more or less unaltered sulphides of the metals, together with some unaltered tungsten compounds and minor amounts of other mineral products. The volatile products, particularly arsenious oxide, are sometimes collected and recovered in bag houses or other dust-collecting equipment.

Some of the associated minerals are broken away from the cassiterite and freed from it by the roasting treatment. When the calcined material is further treated by mechanical concentration methods, some of the altered or separated minerals are removed, producing purer and cleaner cassiterite concentrates.

The roasting of tin concentrates is done in roasting furnaces of many types, more or less following roasting practice used in the metallurgy of the ores of other metals. The roasting may be done in hand-rabbed reverberatory furnaces or in mechanical furnaces of which many types are in use. Perhaps the most popular furnaces for the roasting of tin ore are those of the rotating-cylinder type, such as the Oxland and Hocking, and the White-Howell furnaces. These furnaces are made with a heavy steel or cast-iron cylindrical shell from 30 to 40 ft. long and from 4 to 6 ft. in diameter, lined with fire brick. They are placed in a nearly horizontal position and are equipped

with bearing rings which run on friction rollers. The furnaces are driven by gears attached to the shell, and rotate at fairly low speed.

The charge end is slightly higher than the discharge end, which arrangement causes the material in the furnace to slowly pass through as the furnace rotates. Coal or oil is used for fuel, and the heat is usually admitted at the discharge end.

Roasting furnaces of the fixed-hearth revolving-rabble type are also used; furnaces of this type are the Wedge, Herreshoff, MacDougall, Ridge, Pearce turret, Merton, and other furnaces of similar construction. Most of these furnaces have fixed circular hearths with revolving rabble arms mounted on a central vertical rotating shaft. The rabble arms are fitted with rabbles which slowly stir the charge and carry it around the hearth as the rabble arms revolve. Some of the furnaces of this type have but a single hearth, while others have several hearths, one above another, all operated by the same central shaft. The top of the furnace is sometimes used as a drying hearth to remove the moisture before the charge is fed to the first enclosed hearth. The furnaces are usually built of fire brick, with arched-roof and sometimes arched-floor construction.

The roasting problems involved do not differ materially from those encountered in the roasting of the ores of other metals. The larger multiple-hearth roasting furnaces and the larger rotating-cylinder furnaces have about the same capacity, and about 1 ton of tin concentrates per hour can be satisfactorily roasted in such furnaces. The fuel consumed is from 100 to 300 lb. of coal per ton of tin concentrates roasted. It is generally desirable to crush the ore or concentrates before roasting, and satisfactory results are usually obtained if the material is crushed to pass about a  $\frac{1}{4}$ -in. screen. To maintain proper roasting conditions, it is usually desirable to keep the roasting furnaces at temperatures of 550 to 650°C. The type of furnace, kind of fuel, and roasting cost depend on the location, character of the labor, kind and amount of impurities in the tin concentrates, and other conditions which affect roasting problems in general, and which have been completely described in many metallurgical treatises.

**Roasting Followed by Leaching.**—Instead of mechanical concentration following the roasting of the tin concentrates, the calcined material is sometimes leached with water or acid solution to remove products which have been made soluble by the roasting treatment.

Leaching with water sometimes removes certain soluble compounds, but leaching with dilute acid solutions is more effective, as some of the products formed during the roasting process are readily soluble in acids, although insoluble in water.

**Heating with Sodium Compounds.**—Some tin concentrates contain tungsten compounds, which are not greatly affected by simple roasting. When these compounds are heated with sodium carbonate or sodium sulphate to about 600°C., sodium tungstate is formed. If the process is carried beyond the stage of the formation of sodium tungstate, some sodium stannate is produced, and for that reason an excess of sodium carbonate or sodium sulphate should be avoided.

In this process the tungsten minerals react with the sodium compounds to form sodium tungstate, which is soluble in water and may be removed by leaching the treated material with water in a properly constructed vat. The sodium tungstate may be recovered from the solution by evaporation, and after being suitably purified has a ready market.

The process should be controlled by regulating the amount of sodium carbonate or sodium sulphate so that it will be present in sufficient quantity to combine with the tungsten but will not be present in excess so as to combine with some of the tin.

This process has been used in several localities, but the results have not been entirely satisfactory, and the process is not used to any great extent at the present time. The removal of tungsten minerals by hand picking is perhaps the most satisfactory method and is the one generally used when it is found necessary to remove the tungsten minerals before smelting.

Jennings and Dolan<sup>3</sup> have proposed a method for removing impurities from tin concentrates by heating the concentrates with acid sodium sulphate (bisulphate) instead of salt cake. They state that the cassiterite is not affected by this treatment, and that many of the other impurities are converted to soluble sulphates and may be leached out with water.

**Chloridizing Roast.**—When the tin concentrates are contaminated with sulphides of the other metals, a chloridizing roast, followed by leaching, is sometimes used to purify the concentrates before they are smelted. When the sulphides of many of the common metals are roasted with salt in an oxidizing atmosphere, the sulphur becomes oxidized and combines with the sodium of the salt as sodium sulphate, while the metals combine with the chlorine in the form of chlorides. Cassiterite is practically unaffected by the chloridizing roast.

Comparatively little information has been obtained in regard to the chloridizing of tin ores and concentrates, but in the metallurgical operations carried on in connection with the treatment of the ores of other metals it has been found that the chlorides of some of the metals are fairly volatile, and in the chloridizing roast such metals as bismuth, lead, arsenic, antimony, and silver may be partly removed in the form of fume. The chlorides of some of the metals which remain with the calcined concentrates are soluble in water or dilute acid and may be removed by suitable leaching and washing.

Leaching of the calcined concentrates with water or dilute acid is usually done in wooden vats, properly constructed, and, in some cases, fitted with filter bottoms in a somewhat similar way to the percolating tanks used in cyaniding gold ores.

The chloridizing roast is carried on in furnaces similar to those used for dead roasting, the principal difference being that from 1 to 5 per cent of salt (NaCl) is mixed with the ore or concentrates before they are charged to the chloridizing furnace. (See the chapter on Chlorine in Metallurgy, this book, for further information on this subject.)

**Oil Flotation.**—The separation of metal sulphides from other minerals by means of oil flotation has been perfected in connection with the metallurgy of other metals and has promising application in the purification and preparation of tin ore or concentrates for smelting. The sulphides of most of the common metals are easily floated under proper conditions which are not difficult to obtain, and cassiterite is practically unaffected, permitting separation of the metal sulphides from the tin mineral.

In this well-known process the finely ground ore is mixed with water and is violently agitated. Oil in small amount, sometimes only a fraction of 1 per cent, is added, and the agitation is continued until a heavy froth forms and floats on the surface. Minute globules of oil become attached to the small particles of metal sulphides because of some special affinity or surface-wetting property of the oil for sulphide minerals, and in this way the oil brings the particles of sulphide minerals to the surface and causes them to float in the form of a froth. This action produces a separation of the metal sulphides from the cassiterite and gangue, which sink in the water in which the flotation is carried on.

Different kinds of oil are used for different sulphide minerals, and, by judicious selection of the oil and certain chemical additions to the water in which the flotation is carried on, not only complete flotation of practically all of the sulphide minerals is obtained, but it is even possible to produce a selective flotation which removes one or more sulphide minerals and leaves the other sulphides unfloatable. A further change in conditions renders additional sulphide minerals subject to the flotation action, and they may then be removed as separate concentrates.

In the past, flotation has not been extensively used in preparing tin ores or concentrates for smelting, but the process is directly applicable to such work and may assume considerable importance in the future.

**Summary of Ore-preparation Methods.**—The common metals which, in the form of sulphides, are often associated with cassiterite and remain as impurities in cassiterite concentrates are Pb, Bi, Sb, Zn, Cu, and Fe. Arsenic is often present in the form of arsenides or arsenates of iron or other metals. Tungsten, when present, is usually in the form of tungstate of lime or other bases.

Mechanical concentration removes the gangue, but usually does not successfully remove the metal sulphides, because the specific gravities of most of the metal-sulphide minerals are not sufficiently different from the specific gravity of cassiterite to make mechanical separation possible.

Roasting will remove most of the sulphur and arsenic in the form of sulphurous and arsenious anhydrides, converting the metals with which they were previously combined into oxides. The sulphides of iron, copper, bismuth, and zinc are converted to oxides by roasting, and sulphide of lead is largely converted to sulphate. After roasting, the oxides of bismuth, zinc, and copper may be removed by leaching with dilute acid. Tungsten may be removed by heating with sodium carbonate or sodium sulphate, followed by leaching with water. Lead, bismuth, antimony, and silver may be removed by a chloridizing roast, followed by leaching with acid. Practically all of the metal-sulphide minerals may be removed by oil flotation. It will, therefore, be seen that a suitable selection of one or more of the purification methods, which have been described, will enable the metallurgist to remove most of the metal impurities contained in the tin concentrates and prevent their reduction with the tin in the smelting operation.

Tin is a high-priced metal, and, in comparison with some of the other common metals, the production of tin is small. No very large tonnage of tin ore or concentrates is smelted at any one tin-smelting plant.

The tin ores or concentrates are usually shipped from the mines in sacks and are sampled before going to the storage bins or to the treatment or smelting departments. It is the usual practice to sample each lot by taking each tenth sack and reducing the sample so obtained by coning and quartering or with a mechanical sampler until a sample of suitable size for assay is obtained.

Because the tin is so valuable, the concentrates must be carefully handled to prevent loss of dust in sampling, during transfer to the storage bins and while charging to the roasting and smelting furnaces.

**Smelting.**—The tin metallurgist is fortunate in receiving the tin in the form of oxide instead of in the form of more complex compounds which would probably introduce metallurgical difficulties. The reduction of tin from its oxide to its metallic form is not difficult, as the reduction takes place readily when tin oxide is heated to fairly high temperatures in the presence of reducing agents, such as carbon. An excessively high temperature is not required to bring about the



reduction of the tin to the metallic form. The temperature required for smelting is largely determined by the composition of the slags which are formed, as the smelting temperature must be such as to produce liquid slags which will permit the reduced tin to settle and collect in the bottom of the furnace.

The smelting of tin offers problems similar to those encountered in the smelting of ores of other metals, and the general statement might be applied to all reduction smelting of this type that the results are always better if the smelting temperature is reached as quickly as possible.

Two distinctly different smelting methods are followed, and the two methods make use of furnaces of entirely different types. In one method the tin concentrates are smelted in shaft or blast furnaces, and in the other they are smelted in reverberatory furnaces. The older method and the one which was in most general use during the early life of the tin-smelting industry of the world is shaft- or blast-furnace smelting.

Reverberatory smelting of tin ores and concentrates did not come into use until well along in the eighteenth century and did not reach full development until the middle of the nineteenth century.

In the smelting of tin ores and concentrates the end desired is to produce as much reduced metal as possible and to make slags of such composition that they will be liquid at the smelting temperatures and permit the reduced tin to settle through them.

It is also desired to produce slags as low in tin as possible, as the principal loss in tin smelting is in the tin carried away by the slags, but the making of low-tin slags is not of the greatest importance in the first or primary smelting of tin ores or concentrates.

Tin smelting does not differ materially from the smelting of the ores of other metals, except that the reduction is simpler, and, because of the absence of appreciable quantities of sulphur, matte is not formed. The smelting of tin would appear to be a fairly simple process, and, as far as the actual smelting operation is concerned, the process is not complicated. The great difficulty in tin smelting is introduced by the fact that tin oxide combines readily with silica to form silicates of tin, and during the smelting of tin concentrates mixed with flux and fuel a considerable amount of tin invariably combines with silica and goes into the slag in the form of readily fusible silicates of tin mixed with the other more or less complex silicates which make up the slag. On the other hand, if an extremely basic slag should be used, tin will act as an acid, and again enter the slag.

In smelting ores of lead and copper, it is comparatively easy, with the production of metal, matte, and slag in the case of lead smelting, or with matte and slag in the case of copper smelting, to hold practically all of the lead and copper in the metal or matte, as the case may be, and prevent it from going into the slag. In tin smelting, however, while a large proportion of the tin is reduced and recovered in the form of metal, an unduly large amount invariably fluxes with silica and goes into the slag. The amount of tin contained in practically all slags from the primary smelting of tin concentrates is so extremely high that such slags cannot be discarded but must be retreated for their tin contents. As it is necessary to resmelt the first-run slags, it is important to use only a small amount of fluxing material in the smelting of tin concentrates so as to produce a minimum amount of slag.

The smelting of tin, therefore, embraces three distinct stages: the primary smelting of the tin concentrates in a blast furnace or in a reverberatory furnace with the proper addition of fluxes and fuel; the retreatment of the first-run slags to recover the tin which they contain; and, finally, the refining of the reduced metallic tin to remove the metal impurities which are reduced with the tin in the smelting process.

**Smelting in the Blast Furnace.**—Historical records seem to show that tin was first recovered by smelting cassiterite in small, crude, hand-operated shaft furnaces which required some draft. Natural draft was probably used in some of the early furnaces, and later on forced draft, created by hand-operated blowers, was introduced.



FIG. 5.—Small Chinese blast furnace.

Some very crude small furnaces are still in use in the Far East, where fairly pure cassiterite mixed with charcoal is fed into small shaft furnaces. No scientific attempt is made to produce slags of any particular composition, and the amount of impurities

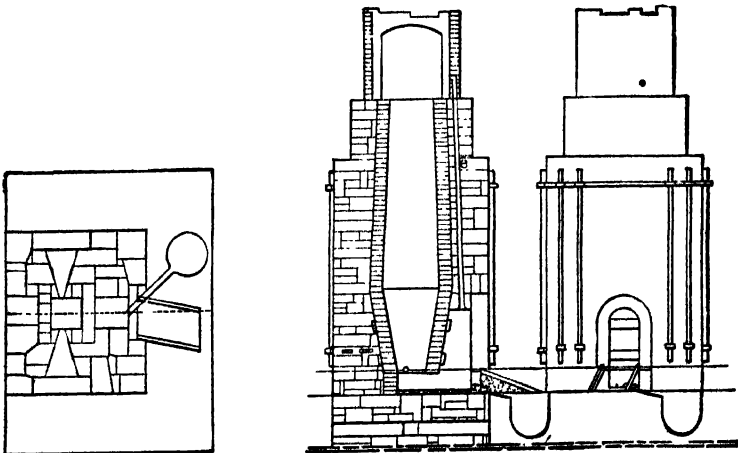


FIG. 6.—Cornish tin castle.

in the ore which is being treated is so small that fairly high reduction of metallic tin is obtained.

Some of the original shaft furnaces used in the Far East were simply hollow pits dug in the ground. The blast for such furnaces was often obtained by means of hand bellows. Some of the smaller Chinese shaft furnaces consist of bamboo forms

lined with clay. A small Chinese tin-smelting furnace operated with a hand blower, such as is still being used in many semicivilized portions of the Far East, is shown in Fig. 5.

With the introduction of the tin ores from Cornwall, the metallurgy of tin in England received much scientific thought, and a large amount of metallurgical skill was devoted to it. The crude furnaces used in the Far East were soon replaced by larger furnaces, and the old familiar blast furnace (known as the "Cornish tin castle") was developed. This was a shaft furnace constructed entirely of stone or brick, and, in its best form, was operated with positive blowers of the Roots type. Charcoal was largely used for the fuel during the early development of tin smelting in England, but was later replaced by coke. The shafts of these furnaces were fairly low, and the furnaces had comparatively small capacity. A typical "Cornish tin castle" is shown in Fig. 6.

At the present time some modern steel water-jacketed blast furnaces are in use in different parts of the world where tin concentrates are smelted in shaft furnaces. The blast furnaces have a fairly low shaft, and are operated with comparatively low blast pressure. With the exception of the low shaft, the furnaces are of the modern lead-smelting type, and metal and slag are produced according to regular blast-furnace smelting practice.

Blast furnaces for the smelting of tin concentrates are operated with coke fuel, and are fluxed with limestone, silica, and other materials to produce easily fusible slags similar to the slags made in the smelting of the ores of other metals.

The charging, fluxing, and operation of tin blast furnaces correspond approximately to similar operations in the blast-furnace smelting of other metals. The principal difference between tin smelting and the smelting of other metals is in the tin which the slags contain.

While the formation of tin silicates as part of the slags is an economic difficulty, it does not introduce any metallurgical troubles, as the silicates of tin have low melting points and do not hinder the satisfactory operation of the furnace. Slags made in blast furnaces smelting tin concentrates are usually high in tin and may often contain from 10 to 25 per cent of tin in ordinary practice.

A brick-lined settler or forehearth is sometimes used to collect the slag and metallic tin as they are tapped from the blast furnace. The slag usually overflows from the settler into slag pots, which are taken away, and the slag is poured into water to granulate it while still molten, or the slag is removed after it has become solid, and is broken up and reserved for retreatment, to recover the tin which it contains.

At intervals the reduced metallic tin is tapped from the bottom of the settler and is run into cast-iron molds. The pigs or slabs of tin are removed from the molds and are taken to the refinery for further treatment to remove the metallic impurities which the tin contains.

Alexander<sup>4</sup> has proposed a modification of the blast-furnace smelting of tin concentrates in which the concentrates are first sintered with from 7 to 10 per cent of coal. The sintering operation is said to remove about 70 per cent of the sulphur and to leave the sintered material in the form of a cake which may be easily broken. The sintered material is fed into a blast furnace with coke and, if desired, some slag which must be resmelted for the tin which it contains. The claim is made that, by using this process, slags low in tin and reduced metal low in impurities are obtained.

**Smelting in Reverberatories.**—The use of reverberatory furnaces for the smelting of tin concentrates dates back to the early part of the eighteenth century, when reverberatory tin-smelting furnaces were introduced into Cornwall. From that time on they came more and more into favor until at the present time most of the modern tin-smelting plants in various parts of the world use rever-

beratory furnaces, not only for the primary smelting of tin concentrates, but also for retreating the slags to remove the tin which they contain.

By the use of reverberatory furnaces instead of blast furnaces it is possible to make somewhat cleaner slags in the original smelting of tin concentrates as well as in the resmelting of first-run slags, and the metallurgical operations are more readily controlled. Because tin is such a valuable metal, it is important to reduce the dust losses as much as possible, and reverberatory furnaces are particularly suited to the smelting of fine tin ores and concentrates, as the dust losses in reverberatory smelting are much less than in blast-furnace smelting.

The reverberatory furnaces generally used for tin smelting are constructed of fire brick and vary greatly in size, the largest of them having a hearth about 30 ft. long

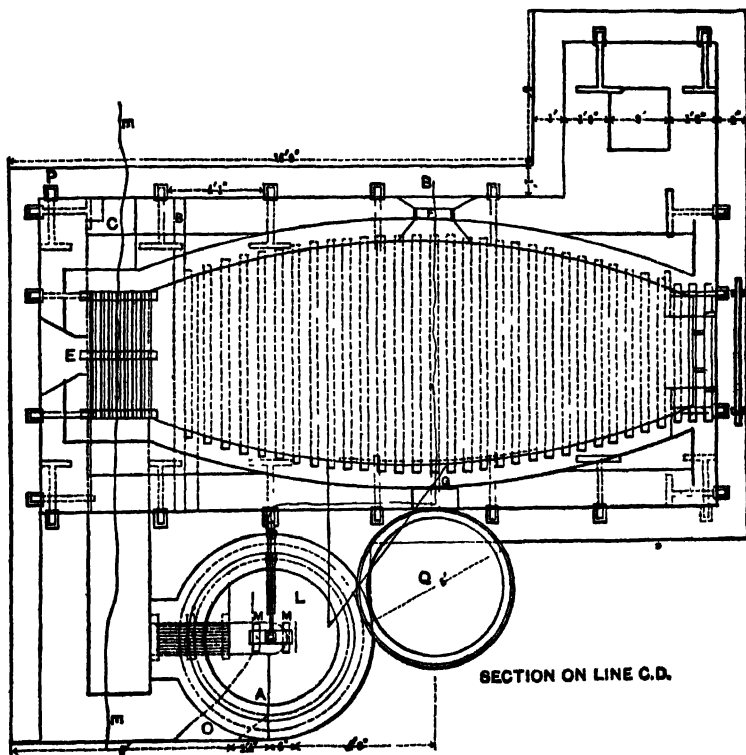


FIG. 7.—Sectional plan, Cornish reverberatory tin furnace.

and 12 ft. wide. They usually have the fire box at one end of the furnace and the flue at the opposite end. Long-flame bituminous coal is usually used for fuel, although oil is an excellent fuel for reverberatory smelting of and very satisfactory results may be obtained with it where the cost is not prohibitive.

A typical Cornish reverberatory tin-smelting furnace is shown in Figs. 7, 8, and 9.

The larger furnaces will take from 8 to 12 tons of charge in each batch. The charge consists of tin concentrates with 15 to 20 per cent of anthracite screenings and small amounts of sand, limestone, slag, and refinery by-products. The charge is well mixed before it is fed to the furnace, and the process is a batch operation, a complete charge being fed to the furnace, smelted, and the furnace tapped before a

second charge is put in. The proper temperature for operating tin reverberatory furnaces is from 1200 to 1300°C. For the larger furnaces 10 to 12 hr. are usually required to smelt each charge.

When smelting tin concentrates, a fairly large amount of tin is allowed to go into the slag, because it has been found that such practice tends to produce reduced metal containing a minimum amount of impurities. The object is not so much to keep the tin out of the slag as it is to keep the impurities out of the reduced tin.

After a batch is smelted, it is tapped from the furnace through a single tap hole, and the reduced metal and slag are allowed to run into a large brick-lined settler or fore-hearth. From the settler the slag usually overflows into cast-iron slag pots which are mounted on trucks and are drawn away on the slag track as soon as they are filled. To remove the slag from the pots the lower ends of bent iron bars are sometimes immersed in the slag while it is still molten, and after the slag solidifies it is lifted from the pots by means of these bars.

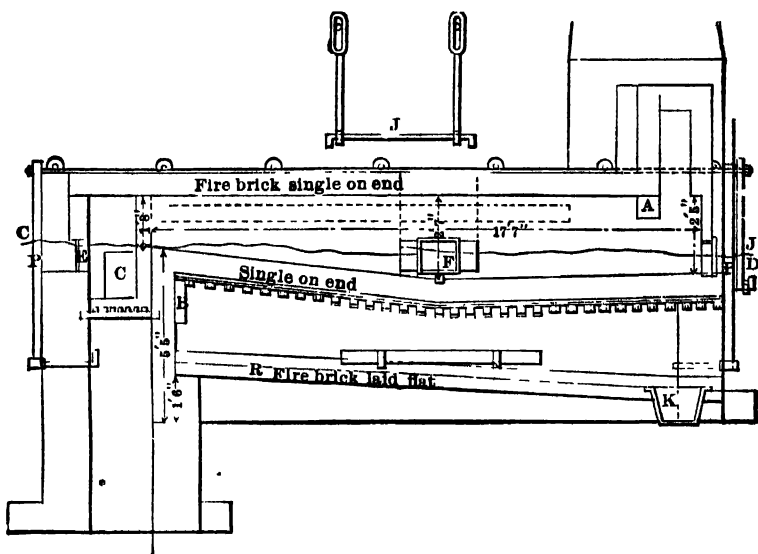


FIG. 8.—Longitudinal section, Cornish reverberatory tin furnace.

Slag obtained from the first smelting of tin concentrates contains so much tin that it should be resmelted, and after the slag cakes are removed from the pots they are to be broken up and crushed to pass about a  $\frac{3}{4}$ -in. ring. The crushed slag is transferred to slag-storage bins, where it is kept until required for slag-smelting charge. Reverberatory-furnace slags, obtained from the first-run smelting of tin concentrates, usually contain from 10 to 25 per cent of tin.

The molten metallic tin is tapped from the bottom of the settler and is cast into pigs or thin flat slabs, weighing about 75 lb. each. The tin is usually cast in the form of slabs, as it has been found that the flat slabs are particularly suitable for charging to the refining furnace.

After the furnace has been tapped, the next charge is immediately introduced before the furnace has a chance to cool. Successful smelting requires that the charge shall be melted as quickly as possible so as to reduce the tin rapidly and prevent it from going into the slag. The charge is stirred at intervals with iron hoes attached to long iron handles which are operated through the side doors of the furnace. The stirring should be deep so as to remove any of the unsmelted charge which adheres to

the bottom of the furnace. As soon as the appearance of the charge indicates that it is completely smelted, the charge should be tapped from the furnace.

Tin-smelting reverberatory furnaces are constructed of fire brick and have a fire-brick hearth sloping toward the tap hole, which is usually placed at about the center of one side of the furnace and low enough to drain the furnace completely when the tap hole is open.

The roof is of arch construction, and, as in other reverberatory smelting furnaces, the roof should be sprung from and supported by heavy continuous steel-beam skew-backs, so that damage to the side walls will not endanger the roof, and side-wall repairs may be made without affecting the roof.

The furnaces are usually charged through several charge holes placed at regular intervals down the center of the furnace roof. The charge material is often kept in small feed bins located above the charge holes, each bin holding enough material for one or more charges, as desired.

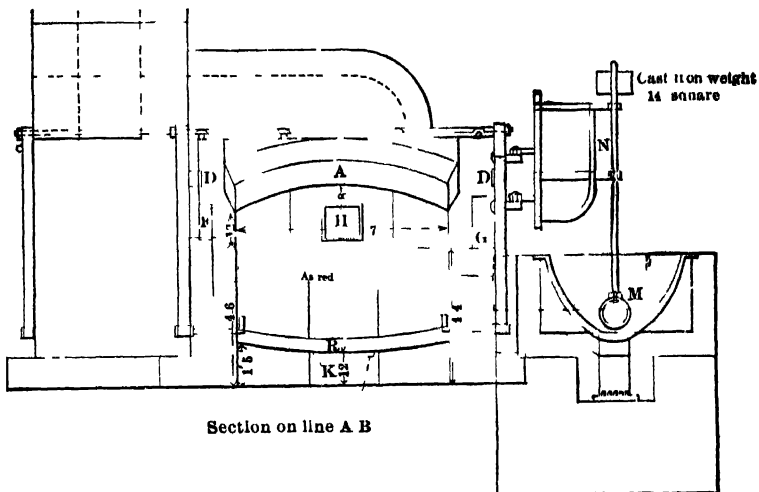


FIG. 9. Transverse section, Cornish reverberatory tin furnace.

Some of the tin compounds are somewhat volatile at the smelting temperatures, and even under the best conditions considerable tin passes out of the furnace in the form of fume and dust. Successful smelting operations require the use of dust-collecting equipment in connection with the smelting furnaces.

**Slag Smelting.**—Slag produced in the first-run smelting of tin concentrates, in either a blast or a reverberatory furnace, invariably contains so much tin that it is necessary to retreat it before it may be thrown away. First-run tin slag is retreated in either a blast furnace or a reverberatory furnace of the same general type as is used for the smelting of tin concentrates.

The cost of smelting slag in a blast furnace is probably somewhat less than in a reverberatory furnace, but the second-run slag obtained from a blast furnace usually contains more tin than similar slag made in a reverberatory furnace.

In smelting slag the main object is to reduce to the metallic form the tin which is contained in the original first-run slag in the form of tin silicates. Generally speaking, a higher temperature is required for slag smelting than for the smelting of tin

concentrates, because it is more difficult to reduce tin to the metallic form from the silicates of the slag than from the oxide in the concentrates.

A fairly large amount of reducing material is required in the smelting of slags, and, when reverberatory furnaces are used, the reducing material is usually added to the charge in the form of anthracite screenings. Some limestone is usually added as a fluxing material. Sometimes metallic iron in the form of scrap or other readily obtainable material is added to the slag-smelting charge to replace the tin in the silicates of the slag and to permit the reduction of the tin to the metallic form. Lime is sometimes depended on to react with the tin silicates to bring about the same result. Metallic tin produced in the smelting of slags is usually very impure and generally contains a large amount of iron in the form of the tin-iron alloy, known as "hard head."

The removal of the tin from the first-run slag is one of the most difficult operations which the tin metallurgist encounters, and successful slag smelting requires great care and expert control. Unless the slag-smelting operations are carefully conducted, the second-run slags will be high in tin.

In the best practice, the slag resulting from the slag smelting should not contain more than 1 per cent of tin, but second-run slags often contain more than 1 per cent of tin, and not infrequently slags containing 3 per cent or more are discarded.

Generally speaking, the metallic tin produced in the smelting of slag, and also the metallic tin produced in the primary smelting of tin concentrates, require some refining before they are ready for the market.

Some of the richer slags from the first smelting of tin concentrates, and also by-products from the refinery and from slag smelting, are returned to the tin-concentrate smelting furnace and are added to an original tin-concentrate smelting charge.

When reverberatory furnaces are used, from 16 to 18 hr. are required for smelting a slag charge. Slag smelting in reverberatory furnaces is a batch process, the same as tin-concentrate smelting, an entire charge being smelted and tapped from the furnace before the next charge is put in. Reduced metal and slag are handled in settlers and slag pots in a manner similar to the handling of such materials from a tin-concentrate smelt. The slag is removed from the pots and is broken up and thrown away, or is poured over the dump while still molten.

**Refining.**—Most of the reduced tin obtained in the smelting of tin concentrates or slag must be refined before it is ready for the market. The tin obtained from the first smelting operation contains many metallic impurities which were reduced with the tin and are alloyed with it. The kind and the amount of impurities which the tin contains depend largely on the metal impurities in the original tin concentrates, and, for that reason, the tin obtained from the smelting of some tin ores requires much more refining than does the tin from other ores.

Two methods of refining tin have been used extensively and successfully. In the first of these methods the tin is refined by heat treatment, and in the second by electrolytic treatment.

The heat-treatment method is the method generally used in various parts of the world, and, although many modifications have been adopted in different places, tin is refined in substantially the same manner in the different localities.

The refining may consist of one or both of two operations: The first is liquating or sweating; and the second, boiling, tossing, or poling. Where both liquating and boiling are necessary, the tin is always liquated first and is then subjected to the boiling treatment. Liquating is done in a comparatively small sloping-hearth reverberatory furnace built with the fire box at one end and the flue at the other. The hearth usually slopes to one side toward a large door or tap hole, which discharges continuously into

either one of two outside cast-iron kettles. A Cornish liquating furnace is shown in Fig. 10.

The object of liquation is to remove from the tin all metallic impurities, alloys, and compounds which have melting points appreciably higher than the melting point of tin, and by this process the tin is separated from the metallic impurities by liquating or sweating it at a temperature just slightly above its melting point.

The bars, pigs, or slabs of tin obtained from the first smelt are placed on the upper side of the liquating-furnace hearth. The furnace is kept at a temperature just

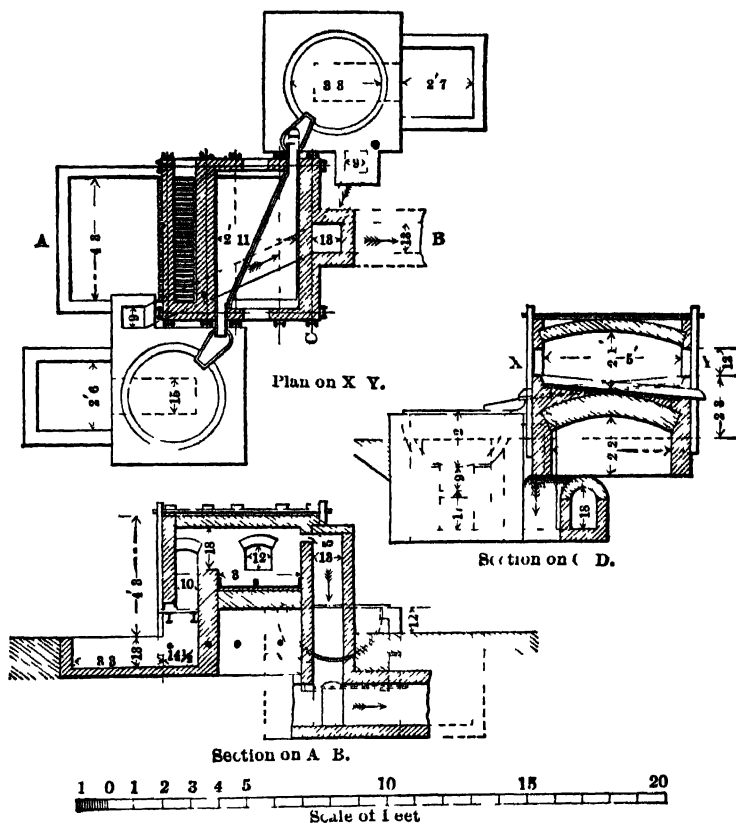


FIG. 10.—Cornish liquating furnace

slightly above the melting point of tin, a slow fire being used for this purpose. Long-flame bituminous coal is used for fuel, and the temperature is carefully regulated.

The bars or slabs of tin are piled on each other with spaces between them, and the tin soon begins to melt and run down. The melting is slow, as the success of the operation depends on careful regulation of the temperature so as not to melt the metallic impurities which are present in the form of alloys and compounds associated with the tin.

The clean tin runs from the furnace into one of the outside kettles, leaving the residue on the hearth. After the metal which melts at a low temperature has been sweated out, the dross remaining in the furnace is pushed toward the fire, and the temperature is raised until all possible metal has been removed. This second sweated



metal is caught in the other kettle, as it is so impure that it should not be mixed with the metal obtained from the first sweat. The second metal is cast into pigs or slabs and is resweated with the next charge.

After the second metal has been sweated from the dross, the temperature is again raised and the dross is thoroughly roasted. The final roasted residue is resmelted with an original tin-concentrate charge in the tin-concentrate smelting furnace.

Many impurities are removed in the liquating furnace, but some of them which have comparatively low melting points are sweated out with the first sweat metal. Most of the iron is removed in the liquating furnace as it remains with the dross, but a small amount goes into the sweated tin. Most of the lead and bismuth also go into the tin. Much of the arsenic, antimony, and copper remain with the dross.

The first sweat tin which collects in the cast-iron kettle outside the liquating furnace is usually boiled or tossed to complete the refining. The kettle holds from 6 to 10 tons of metal and is usually separately heated by a coal fire underneath it. The metal in the kettle is heated to a temperature considerably above its melting point, and the boiling operation is carried on by stirring the molten metal with a pole of green wood or by immersing in it a bundle of green-wood sticks held together by iron bands. At the high temperature of the metal the green wood undergoes destructive distillation, and the steam and gases resulting from the distillation of the wood are given off beneath the surface of the metal and produce a strong boiling or bubbling action in the bath. (Cf. Copper Poling, p. 961.) In this way the different portions of the metal bath are brought to the surface and exposed to the air. Some of the metal impurities and part of the tin are oxidized, and the oxide drosses collect on the surface and are skimmed off from time to time. These drosses are resweated or are smelted with an original tin-concentrate smelting charge in the same way as the residues from the liquating furnace. In some of the more modern refineries the boiling is done by agitating the molten metal with compressed air instead of green-wood sticks.

The boiling operation is carried on until the desired grade of refined metal is obtained. If the tin contains fairly large amounts of impurities, the boiling is sometimes continued for many hours. The metal must not be heated to an excessively high temperature, as boiling at a high temperature causes a large amount of the tin to become oxidized.

Tossing consists in filling hand ladles with the molten tin and pouring the molten metal back into the kettle, thus exposing it to the oxidizing action of the air. Tossing produces oxidized drosses similar to the drosses which form in the boiling operation. Boiling is the method usually used, and both tossing and boiling are hardly ever employed at the same refinery.

Iron is almost completely removed by the boiling operation, and other impurities, principally arsenic and antimony, are greatly reduced in amount.

After the refining has been completed and the dross has been skimmed from the kettle, the surface of the metal will have a clean bright appearance, and the tin is then removed, usually by hand ladles, and is cast into pigs ready for the market. Great care is exercised in casting the pigs so as to give a fine appearance to the metal. Tin tends to oxidize on the surface while in the molten condition, and for that reason the metal is poured at a temperature just slightly above its melting point. The metal is poured into cast-iron molds, which are filled quickly and are skimmed lightly on the surface with a wooden paddle just before the metal solidifies.

The electrolytic refining of tin has been successfully used at one refinery in the United States, but, because of economic conditions previously discussed in this book, tin smelting and refining in the United States were abandoned in 1923 and, with the closing down of this American electrolytic-tin refinery, the electrolytic-refining process is no longer used to any extent.

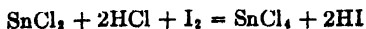
As in the electrolytic refining of other metals, many impurities originally contained in the tin are removed by this process, and very pure tin is produced. Because of the possibility of removing the metallic impurities from the tin, it is not so essential, when electrolytic refining is to follow the smelting operation, to remove the other metal minerals from the tin concentrates before smelting. The refining is carried on in the usual way in electrolytic cells, tin being deposited on the cathode and minor amounts of other metals being recovered in the form of by-products. The patents state that, as originally developed, the electrolytic tin-refining process made use of an electrolyte of hydrofluosilicic acid containing sufficient sulphuric acid to combine with the lead present to form lead sulphate. In the later modifications of the electrolytic-refining process, the electrolyte consisted of hydrofluosilicic acid containing some sulphuric acid, a small amount of cresylic acid, and glue. The hydrofluosilicic acid used was of about 15 per cent strength and had about 4 per cent of tin dissolved in it.

Vail<sup>6</sup> states that at the American refinery where this process was used the refining was done in sixty-eight tanks similar in size and construction to those used for copper refining. The tanks were of wood construction and were lined with asphaltic material. Hard-rubber fittings were used for the pipe lines, which carried the electrolyte. Each tank contained about 11,000 lb. of tin anodes, and the cathode starting sheets were of tin  $\frac{1}{8}$  in. thick. The current density was about 12 amp. per square foot, and the deposition per ampere-hour was about double that of copper. Vail also states that, before being cast into anodes, the tin obtained from the smelting of tin concentrates was first subjected to refining by liquating and boiling. A general description of the process is given in the patent specifications.<sup>6</sup>

**Methods of Assay and Analysis.** There are two general methods in use for determining the amount of tin in ores and other products; the fire assay and the volumetric wet analysis.

The fire assay for tin is usually conducted in the following manner: Grind slightly more than 5 g. of the sample until it will pass through a 100-mesh screen. Dry at 100°C., cool, and weigh out exactly 5 g. into an 8-oz. wide-mouth flask. Add 100 c. c. hydrochloric acid (concentrated) and digest at a low heat until the volume is reduced to about 15 c. c. Add 50 c. c. nitric acid (concentrated) and continue the evaporation to a volume of 10 to 15 c. c. Add about 200 c. c. of water, boil, and allow to stand. Filter on double filter papers containing paper pulp, washing with warm water just acid with nitric acid. If tungsten is present, treat with ammonia (concentrated) and again filter and wash with water. Transfer the precipitate to a porcelain crucible and ignite. Brush the contents of the crucible onto a clean sheet of glazed paper, break up lumps with a spatula, mix thoroughly with 20 g. of sodium cyanide (free from chlorides), and transfer to a 20-g. clay crucible in which has been placed 4 or 5 g. of sodium cyanide. Cover with sodium cyanide, fuse in a muffle furnace at a red heat for from 20 to 25 min., cool, wash with water, break crucible to obtain the button, clean the button, and soak in hot water to remove adhering cyanide. Dry and weigh. Run in duplicate. Duplicates should agree within 0.15 per cent.

The volumetric determination of tin is very useful and is applicable to nearly all kinds of ores, metallurgical products, and other materials containing tin. A number of volumetric methods have been proposed, the best of which depends on the titration of stannous chloride with standard iodine in cold hydrochloric acid solution. This is called the Pearce-Lowe method,<sup>7</sup> and is one of the simplest, shortest and most accurate for the volumetric estimation of tin. It depends on the oxidation of stannous to stannic chloride by iodine in cold hydrochloric acid solution according to the equation.



Starch solution is used as indicator. A small amount of sulphuric acid is not objectionable, but nitric acid and nitrates must not be present.

The method requires that the tin shall be brought into solution in hydrochloric acid. When possible, the finely ground sample is dissolved directly in hydrochloric acid; in some cases the addition of a small quantity of potassium chlorate, antimony chloride, or platinic chloride, or the presence of a piece of platinum foil, accelerates solution. In the analysis of materials containing sulphides or certain alloys, a mixture of hydrochloric and nitric acids may be used, followed by treatment with sulphuric acid and then with hydrochloric acid. Siliceous products frequently respond to treatment with hydrofluoric acid.

For the decomposition of insoluble silicates, fusion with alkali carbonates is effective. Practically all silicates are decomposed by this process, but it is not suitable for use with samples containing insoluble tin oxide, and if sulphides or salts of tin soluble in acids are present they should be removed before the fusion process is applied. The addition of 10 per cent of borax to the alkali carbonate accelerates the decomposition in some instances.

Acid-insoluble residues may be decomposed by fusion with sodium or potassium hydroxide, the melt being subsequently dissolved in hydrochloric acid. This method is perhaps the most useful of the fusion processes; since it is applicable to almost all products and generally requires only a very simple preliminary acid treatment. An iron crucible is the most suitable for use with this process.

Sodium peroxide may also be used for the fusion process, but it corrodes the crucibles very rapidly, and generally its disadvantages more than offset the extra speed gained by its use. The addition of organic matter to the peroxide, to furnish the necessary heat for the reaction, has been suggested as a means of preventing the corrosion. Quieter fusion results if zinc sulphide, iron sulphide, or potassium persulphate is added to the peroxide.

In the final hydrochloric acid solution, the tin will usually be found in the stannic condition and must be reduced to the stannous condition before titration. This reduction is usually accomplished in one of four ways: by the use of iron in the form of rods; nickel or aluminum in the form of sheets or strips; or finely powdered antimony. Only pure soft iron may be used. If carbon is present in the iron, it will generally cause high results.

The use of aluminum renders this part of the method somewhat uncertain and makes it difficult to control the operation. The principal objection to the use of antimony is that the presence of so much finely powdered material in the solution obscures the end point. The only objection to nickel is the light-green color given the solution, but this does not affect the sensitiveness of the end point if the concentration of nickel salts is only that derived from the metal used for the reduction.

The reduction and the titration are best performed in an atmosphere of carbon dioxide and in a solution containing not less than 25 per cent nor more than 40 per cent by volume of free concentrated hydrochloric acid. The temperature of the solution to be titrated should not exceed 22°C.

One-half to 2 g. of the sample (depending on the percentage of tin) is first brought into hydrochloric acid solution. The solution is transferred to a 12-oz. wide-mouth conical flask; enough concentrated hydrochloric acid is added to make a total of 50 c.c. of free concentrated hydrochloric acid present, and the solution is diluted to 200 c.c. with water. A nickel coil is prepared by rolling 6 sq. in. of heavy sheet nickel (4 in. long and 1½ in. wide) into a loose roll of such size that it may be easily inserted into the flask. A narrow strip of nickel is left attached to one side of the coil, long enough to reach above the top of the flask. This coil is placed in the flask containing the tin solution; the nickel strip is bent over the edge, and the flask is covered with a small watch glass. The solution is heated to boiling and gentle

ebullition is maintained for 30 min. after all the iron, which is present, is reduced. The reduction of the iron is indicated by the yellow color of the solution changing to a pale green. Thirty minutes is more time than is necessary for the complete reduction of the stannic chloride from 0.5 g. of tin oxide, and if complete reduction does not result in that length of time either the nickel coil is too small or the nickel is inactive, due to impurities, and should be discarded and replaced by pure nickel.

It has been stated, as an objection to this method, that it is impossible to tell when the reduction of the tin is complete and that the operator may titrate the solution before the tin is all in the lower form. It has been found that larger amounts of tin than would ever be taken as a sample are entirely reduced long before the expiration of the time allowed for the reduction, and no trouble need be anticipated from this cause.

The solution in the flask is cooled in an atmosphere of carbon dioxide generated by adding two  $\frac{1}{2}$ -in. cubes of crystalline marble to the solution. The nickel coil is then removed and is washed with cold hydrochloric acid solution (1 of concentrated acid to 3 of water) as it is withdrawn from the flask. A small amount of starch solution is then added and the solution titrated at once with standard iodine.

The standard iodine solution most convenient for this titration is prepared by dissolving 10.7 g. of iodine in 50 c.c. of water containing 20 g. of potassium iodide in solution and making up to 1 l. with water. When a half-gram sample is taken for analysis, 1 c.c. of this solution will equal 1 per cent of tin. It may be standardized against tin or arsenious oxide.

Few of the elements which are ordinarily found in materials to be analyzed for tin interfere with this method. Ni, Co, Mn, Mo, Ur, Cr, Al, Zn, Pb, Ca, Mg, sulphates, phosphates, bromides, iodides, and fluorides have no effect unless present in such large amount that their color masks that of the indicator. Arsenious and antimonious compounds in weak acid solution consume iodine, but in a hydrochloric acid solution of the strength used in this method they have no effect.

If about 0.1 g. or more of antimony is present in the solution, the nickel coil will precipitate metallic antimony in a very slimy condition which does not settle and obscures the end point. This may be prevented by using a solution containing more hydrochloric acid. If, therefore, the sample taken contains 0.1 g. or more of antimony, the solution is made up to contain 75 c.c. of free concentrated hydrochloric acid instead of 50 in 200 c.c. of volume, before reduction. If this is done, the precipitation of slimy antimony will be prevented and no trouble will be experienced. If the antimony content is not known and the slimy antimony begins to precipitate during the reduction, an additional 25 c.c. of concentrated hydrochloric acid may be added, which will generally cause the antimony to dissolve and prevent further precipitation. If the precipitated antimony does not dissolve, another sample can be treated, adding more hydrochloric acid before reduction.

Copper in small amounts has no effect on the method, but if 0.05 g. or more are present in the solution it will be incompletely precipitated during the reduction, the titration will consume more iodine than is required by the tin, cuprous iodide will be precipitated, and the results will be erratic and high.

If copper is present in the sample in large enough amount to interfere, it must first be removed by treatment with nitric acid.

Bismuth is precipitated in the metallic form during the reduction with nickel. In this form it is said to consume iodine slowly, but the action is slight, and, unless present in large amount, its effect is negligible. If it is desired to remove it, the metallic precipitate may be filtered and the filtrate again reduced and finished as usual.

Tungsten is reduced by the nickel coil to a lower state of oxidation, with the formation of a blue precipitate, said to be  $W_2O_4$ . This is said to be slowly oxidized by

iodine, thus giving high results, but the oxidation is not proportional to the amount of tungsten present. Tungsten in amounts usually met with does not interfere to any extent, and its effect is only noticeable when it is present in large quantity. In case it should be desirable to separate the tungsten, the blue oxide may be filtered off with the precipitated bismuth, the solution afterwards being again reduced and titrated.

Titanic chloride is reduced to titanous chloride by the nickel coil. In the Pearce-Lowe method titanium alone or with iron is said to consume no iodine, but in the presence of tin large amounts of titanium will consume iodine, giving high results. The error caused by titanium seems to be approximately a constant one and is independent of the amount of titanium present. Titanium may best be removed by converting the tin to insoluble oxide by evaporation with nitric acid and then fusing for 5 min. with potassium bisulphate. The melt is dissolved in water and sulphuric acid and filtered.

If titanium and tungsten are both present, the tungsten will remain with the tin after filtering the extracted melt of the bisulphate fusion. The tungsten may be removed from this residue by heating with ammonium carbonate solution, in which the tin is insoluble.

Neither bismuth, tungsten, nor titanium, in any reasonable amount, such as is usually met with, interferes with the method, and they may, in general, be neglected, especially if the titration is performed rapidly, which, to a large extent, will eliminate secondary reactions. The interference of all of these metals is greatly increased by very slow and careful titration, which seems to accelerate their action and give them time seriously to affect the results. This is especially true of titanium, for bismuth and tungsten are not so active and, as a rule, need not be considered.

Ferrous chloride is oxidized only by excess of iodine, and no action takes place unless a very large amount of iodine is run in and allowed to stand. Its action is very slow even then, and the presence of iron does not affect the accuracy of this method.

A tin determination may be run through and results obtained by this method in about 1½ hr., and the method is accurate to about 0.1 per cent.

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- <sup>3</sup> United States patent 1435303.
- <sup>4</sup> United States patent 1426341.
- <sup>5</sup> VAIL, R. H.: *Eng. Mining J.*, May 27, 1916.
- <sup>6</sup> United States patents 1157830 and 1397222.
- <sup>7</sup> *J. Soc. Chem. Ind.*, Nov. 15, 1916.

## CHAPTER XLIII

### MINOR AND RARE METALS

Be, Ct, Ce, Cb, Dy, Er, Eu, Gd, Ga, Ge, Ha, Ho, In, La, Lu, Mo, Nd, Pr, Rb, Sm, Sc, Se, Ta, Te, Tb, Tl, Th, Tm, Ti, Yb, Yt, Zr

**General Considerations.**—The final separation of the rare earths usually depends on repeated fractional crystallizations or precipitations and leachings. The separations are not clear cut, and the spectroscope is the final method of test for purity. The work with the rare metals and earths therefore requires an immense amount of time and patience.

One general separation of the entire group depends on the fact that when tartaric acid, ammonia, and ammonium sulphide are added to the filtrate from the  $H_2S$  group (Fe, Zn, Co, Cr, Ni, V, Al, and Mn will be precipitated (the last two not quite completely,) and in the solution will remain W, Ti, Zr, Th, Be, Ca, Mg, Na, K, Li, traces of Al, and Mn, and the rare earths.)

From this solution, precipitation with oxalates in acid solution, re-solution, and reprecipitation will give only the rare earths in the final residue.

Hopkins gives the following general procedure. <sup>2</sup> The ore is ground to a fine powder and extracted with acid or fused. The acid is usually HCl or  $H_2SO_4$ , although HF is sometimes employed. The fusion mixture may be  $HKSO_4$ , NaOH or HKF. The use of the fluorides is usually limited to minerals containing columbium and tantalum, since the fluorides of these compounds are soluble and hence can be separated from the insoluble fluorides of the rare earths, which can then be decomposed with  $H_2SO_4$ .

The solution is saturated with hydrogen sulphide to throw out the copper-tin group and the rare earths then thrown down with oxalic acid. Both solutions should be boiling and the oxalic acid added slowly.

Thorium and zirconium can be removed by boiling the crude oxalate with ammonium oxalate, which dissolves all the zirconium and most of the thorium. Thorium may be completely removed by repeated treatments with ammonium oxalate, or by precipitation from a neutral or slightly acid solution with  $H_2O_2$ .

Columbium and tantalum if present, are also removed by this means.

The rare-earth oxalates remaining after extraction of the Cb, Ta, Zr, and Th are then separated into the cerium-group earths and the yttrium-group earths. James' method is as follows. Mix the dried oxalates with enough sulphuric acid to form a thick paste, then ignite cautiously. Dissolve the anhydrous sulphates in ice water and sift in solid sodium sulphate. The order of precipitation is approximately Se, La, Ce, Pr, Nd, Sm (the cerium group, sulphates difficultly soluble), Eu, Gd, Tb (terbium group, sulphates slightly soluble), Yt, Dy, Ho, Er, Tm, Yb, Lu (yttrium group, double sulphates very soluble). The separation is not exact, and the yttrium group will begin to come down before all the cerium group is precipitated. Consequently, to obtain the cerium group free from the yttrium group, much of the former must be left in solution. To obtain the yttrium group free from cerium enough alkali sulphate

must be added to precipitate a considerable amount of the yttrium group. If the purification of any members of the yttrium group is purposed it is best to add alkali sulphate until the neodymium absorption lines can no longer be seen.

Cerium itself may be removed by the treatment of a neutral solution with potassium bromate and a few small pieces of limestone. The cerous salts are oxidized to ceric and come down as a basic precipitate.

The cerium-earth double sulphates can be reduced by fusion with charcoal and will then go into solution with hydrochloric acid.

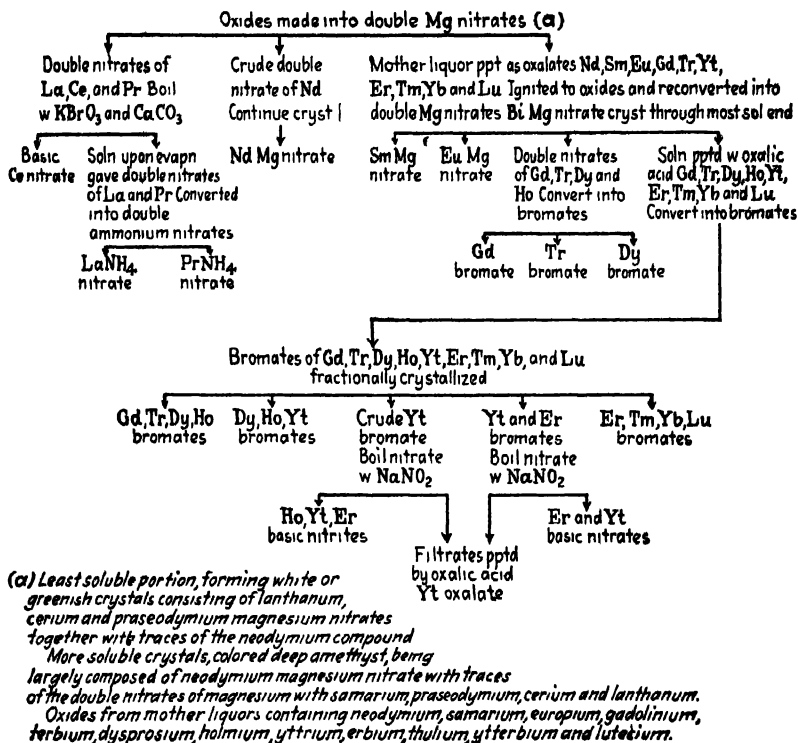


Fig. 1.—Flow sheet of precipitating rare earths

Cerium can also be removed by the James bromate method.<sup>1</sup> In this some small pieces of lime are added to the nitrate solution, to keep it neutral, and then  $\text{KBrO}_3$  is added and the solution boiled. The cerium is oxidized to the quadrivalent condition and precipitates as a basic salt.

If the crude oxalates from the mineral contain less than 20 per cent of the yttrium group it is well to begin fractional crystallization of the nitrates at once. When the yttrium elements in the soluble end of the series become abundant enough to interfere with the crystallization of the cerium group, then the cerium group should be separated with sodium sulphate.

Except for these few general methods, the separations are long-continued fractional crystallizations or precipitations. Urbain and Welsbach sometimes made thousands of crystallizations in the effort to differentiate two of these rare earths. The process of fractional crystallization is very well described by Dr. Moore under Radium (see

p. 1354. A table of comparative solubilities appears below, and James and Pratt's scheme appears on page 1394.<sup>1</sup>

In the more soluble end of the crystallizations it may be necessary at some time to throw down the rare earths as oxalates to get rid of accumulated iron and alumina.

## COMPARATIVE SOLUBILITIES

(The solubility increases from top to bottom)

Double Mg nitrates	Bromates	Double sulphates	Sodium glycolates	Fused nitrates	Dimethyl phosphates <sup>2</sup>
La	La	Sc	Yt	Ho	Yb
Ce	Ce	La	La	Tb	Er
Pr	Pr	Ce	Ce	Sm	Yt
Nd	Nd	Pr	Pr	Gd	Gd
Sm	Sm	Nd	Nd	Lu	Sm
Bi	Bi	Sm	Sm	Yt	Nd
Eu	Eu	Lu	Gd <sup>1</sup>		Pr
Gd	Gd	Gd			Ce
Er	Tb	Tb			La
Yt	Dy	Yt			
Tm	Ho	Dy			
Lu	Yt	Ho			
Ho	Er	Er			
Dy	Tm	Tm			
Tb	Ny	Yb			
	Lu	Lu			
	Ct				
	Sc				

<sup>1</sup> Solubility about twice the Sm salt

<sup>2</sup> The double dimethyl phosphates are much less soluble at 80 or 90°C than at 15 to 20°C

The preparation of the double magnesium nitrates, which are very useful in fractional crystallizations, is carried on as follows: the rare-earth oxides are dissolved in nitric acid, having a slight excess of the oxides present, and then the solution is reduced (chiefly ceric to cerous salts) by means of a little of the original oxalates from which the oxides were derived. A quantity of nitric acid equal to that in which the oxides were dissolved is then neutralized with chemically pure magnesium oxide and the rare-earth and the magnesium solution are then filtered and added together.

Basic nitrates can be made in two ways. The first method consists in converting oxalates into oxides, thence to nitrates, recovering the nitrate as a solid salt, and fusing until decomposition sets in. In dissolving the resultant mass with water the solubility runs: Yt, Eu, Gd, Sm, Tb, Ho, the holmium salts being least soluble.

The second method consists in adding hot caustic soda little by little to a boiling solution of the nitrates.

In general, crystallization should be carried on by two methods used alternately, one of which tends to concentrate the impurities in the crystals and the other in the mother liquors.

<sup>1</sup> Reprinted from *J. Am. Chem. Soc.* (1916), 43



**Aldebaranium**, cassiopeium, denebium, dubhium, and neothulium were the names given to elements which Auer von Welsbach separated from erbium, which he regarded as of complex nature, and from thulium. Later investigators have not confirmed his findings.<sup>1</sup>

**Beryllium.**—For the extraction of beryllium from beryl, H. Copaux suggests the following:<sup>2</sup> Heat the mineral with two parts of  $\text{Na}_2\text{SiF}_6$ , forming  $\text{Na}_3\text{AlF}_6$  and  $\text{Na}_2\text{BeF}_4$ . Crushing followed by lixiviation removes most of the Be with a little Al.  $\text{BeO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$  are then thrown down with boiling  $\text{NaOH}$ , dissolved in  $\text{H}_2\text{SO}_4$  and pure  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  crystallized out. Cb and Ta interfere and must be removed as oxalates.

The separation of beryllium from the other iron-group metals can also be carried out by fusing with sodium carbonate.  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  form soluble compounds that can be leached out.  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and  $\text{BeO}$  stay behind. A fusion with  $\text{HKSO}_4$  then separates the iron and beryllium. While recommended for large-scale use it seems a laboratory method.

The preparation of beryllium from gadolinite is thus described by James.<sup>3</sup> The finely powdered mineral is treated with hot  $\text{H}_2\text{SO}_4$  to dense fumes. The solution is allowed to settle, is decanted, and hot oxalic acid solution added. After filtering off the rare-earth oxalates,  $\text{KBrO}_3$  is added to oxidize the oxalic acid and iron and beryllium precipitated together by adding a little ammonia, then sodium hydroxide, until the odor of ammonia is noticed. Filter. Enough hydrochloric or sulphuric acid is then added to dissolve about two-thirds of the precipitate, and sodium hydrate slowly added until the iron is almost down (as shown by testing a clear portion of the solution) and the solution filtered. The remainder of the iron is then treated with hypobromite solution at boiling, and precipitated with sodium hydroxide until ammonia gives a white hydroxide precipitate with it. The last trace of iron is then thrown out with sodium-hydrogen sulphide and filtered off. (These last two residues contain beryllium and are worked up with the next lots of mineral.) The beryllium is then thrown down as basic carbonate by adding a concentrated solution of sodium carbonate to the solution. The hydrogen sulphide must be boiled out before this precipitation.

Beryllium has been obtained as metal by reduction of the chloride by sodium and potassium, in an atmosphere of hydrogen. Another process is to heat beryllium potassium fluoride with sodium. It has been obtained in lustrous hexagonal crystals by electrolyzing the double fluoride of beryllium and sodium or potassium with an excess of beryllium fluoride. A more recent process electrolyzes a fused bath of sodium and beryllium fluorides with an output of compact metallic beryllium. The metal is 99.6 per cent pure.

It has a silvery luster and when cold flattens easily under the hammer. The specific gravity is 1.79 and the melting point  $1370^\circ\text{C}$ . The metal is insoluble in cold concentrated nitric acid. Its specific heat is 0.4070.

About 0.5 per cent of beryllium is added to the thorium-cerium solution used in incandescent gas mantles to give body to the mantle.

**Cassiopeium.**—See Aldebaranium.

**Celtium (Ct).**—Reported by G. Urbain in 1911 as allied to lutecium and scandium. In properties it lies between them. Gadolinite is its chief source.

**Cerium.**—Except for the pyrophoric alloys and cerium steels (these showing no great advantage over cheaper alloys), this metal has no metallurgical applica-

<sup>1</sup> *Sitzb. Akad. Wiss. Vienna*, **2**, a, 124; *J. Chem. Soc.*, **110** (II), 277.

<sup>2</sup> *Chim. Ind.*, **2** (1919), 914.

<sup>3</sup> *J. Am. Chem. Soc.*, **33**, 875.

tions. There is a steady economic pressure from thousands of tons of accumulated residues in the gas-mantle industry, but no absorption into the arts. While this is due to its price, this could not be permanently lowered because of a true scarcity of cerium in the earth's crust, and any considerable use would immediately reduce supplies to the vanishing point.

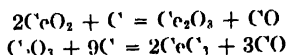
Lanthanum, praseodymium, neodymium, and samarium are the related elements.

Metallic cerium cannot be obtained by electrolysis of the fused salts, except in finely divided condition. Escard<sup>1</sup> recommends electrolyzing a mixture of 3 parts BaCl<sub>2</sub>, 3 parts CaF<sub>2</sub>, 8 parts CaCl<sub>2</sub>, and 10 parts CeCl<sub>4</sub>, heating the mixture in an electric furnace and using an iron crucible as cathode. CeCl<sub>4</sub> is added as the reaction proceeds. At 200 amp. and 15 volts he says a product results containing 98 per cent cerium, 1 per cent iron, and traces of oxide and carbide. The metal can be purified by amalgamation and distillation of the mercury. It has a density of 6.92 and a melting point of 653°C. It is only slowly affected by cold water, but rapidly by hot water, with the evolution of hydrogen. It burns when heated to 160°C. The pyrophoric alloys cerium-magnesium and cerium-aluminum can be obtained by simultaneous electrolysis of the mixed salts. Cerium-iron may be obtained in the absence of air by heating the elements in an electric furnace in a graphite crucible at red heat—cerium 70 per cent, iron 30 per cent is the common alloy.

Metallic cerium cannot be obtained by reduction of the oxide by carbon, as a carbide forms, even in the presence of an excess of the oxide, in which case CeC<sub>3</sub>.2CeO<sub>2</sub> is formed. Formation of the carbide may be prevented by adding CuO, copper-cerium alloys being formed.

The initial separation of the metal from monazite sand is said to be by dissolving the sand in sulphuric acid and adding HNaSO<sub>4</sub> to throw down double sulphates of cerium-group metals and sodium.<sup>2</sup>

In the formation of cerium carbide in the electric furnace the process seems to be a three-stage affair:



and the CeC<sub>3</sub> then breaks down into CeC<sub>2</sub> and graphite, so that it seems impossible to prepare CeC<sub>2</sub> without graphite.<sup>3</sup>

Sebacic acid in boiling aqueous solution precipitates thorium quantitatively, but not cerium or lanthanum. By the addition of bromine water in excess to a suspension of the cerium earths in alkaline solution, followed by heating at 100°C. until the excess bromine is expelled, and then filtering, the filtrate will be freed from cerium and will contain lanthanum and didymium.

Waste material from the gas-mantle industry can be used for the preparation of metallic cerium.<sup>4</sup> The oxides are dissolved in HCl, using an excess of oxides. Sodium and phosphorus compounds are removed with barium chloride and iron, manganese, and chromium by ceric oxide. The solution is then evaporated. The formation of oxychlorides is prevented either by an atmosphere of HCl gas, or by 30 per cent by weight of a mixture of KCl and NH<sub>4</sub>Cl or NaCl and NH<sub>4</sub>Cl is added before evaporation. After evaporation fusion is effected in cast-iron pots high in carbon and silicon, and the fused salt boiled for 20 min. The mixture is then transferred to the electrolytic cell and electrolyzed at 850°C., with an anode current density of 6 to 7 amp. per square inch for graphite and 5.5 amp. for carbon. About 7 to 12 volts pressure is used. If the electrolyte was prepared by the second method, the temperature may be raised to 950°. After the twenty-fourth hour, heat and stir every

<sup>1</sup> *Ind. Chim.*, **5**, 182

<sup>2</sup> U. S. patent 1279257, W. S. Chase.

<sup>3</sup> DAMIENS, A., *Ann. Chim.*, **10**, 330

<sup>4</sup> British patent 119229 of 1918

half hour to agglomerate the cerium, shutting down at the end of about 27 hr. If the electrolyte was prepared by the second method, the process may run 60 hr. The pot which served for the electrolysis is broken up, as it is too much attacked to use again. There are small quantities of lanthanum, dysprosium, erbium, and thorium in the cerium thus produced.

Misch metal can be prepared from the gas-mantle residues without purification. This will ordinarily run 50 to 60 per cent Ce; 25 per cent La; 15 per cent Dy, Sa, etc.; and 1 to 2 per cent Fe.<sup>1</sup>

About 0.3 to 2.0 per cent CeO<sub>2</sub> is recommended in the ThO<sub>2</sub> for gas mantles.

Crude cerium oxalate gives up its iron impurities upon treatment with dilute hydrochloric acid. It can then be converted to hydrate by boiling with KOH or to oxide by calcination. Pure CeO<sub>2</sub> appears to be of a light chamois color.

**Columbium.**—The element, in the form of oxide, is almost invariably associated with tantalum ores, its separation from tantalum being described under the head of that metal. The columbium remains in solution as potassium fluoxycolumbate (2KF.NbOF<sub>5</sub>).

Columbium can be separated from zirconium by fusion with sodium carbonate and leaching with hot water. Columbium dissolves completely, tantalum largely, zirconium not at all.

Metallic columbium can be prepared by electrolysis of the molten fluocolumbate, prepared as given under Tantalum (*q.v.*).

The alloys of columbium are said to be highly acid resistant, two in particular being noted: Zr, 6.8; Cb, 53.5; and Ta, 39.7 per cent (Canadian patent 214118); and Ni, 75; Fe, 11; and Ta and Cb, 14 per cent.<sup>2</sup>

**Denebium.**—See Aldebaranum.

**Dubhium.**—See Aldebaranum.

**Dysprosium.**—This metal was discovered in 1886 by Lecoq de Boisbaudran, who named it for the Greek "difficult to approach," because of the trouble he had in isolating it. The mineral or residue is decomposed with hydrochloric acid and the rare earths precipitated as oxalates and the precipitate washed to remove iron and beryllium. Usually the earths are reprecipitated to remove silicon and iron further. If the cerium group is present, it is best removed by the double-sulphate method. In this, the oxalates are converted to sulphates by moistening with sulphuric acid and ignition to 400°C.; the resulting sulphates dissolved and solid sodium or potassium sulphate added to the solution to saturation, (see p. 1393), most of the cerium group being thrown down in such a solution. The earths in solution should then again be precipitated as oxalates to get rid of the alkali salts.

As the yttrium group are again in solution as sulphates, the metals are converted to bromates by double decomposition with barium bromate. The bromates are then recrystallized fractionally.

LEAST  
SOLUBLE  
Sm, Nd, Pr

MIDDLE  
Dy, Ho

MOST  
SOLUBLE  
Er, Yt, Tm.

<sup>1</sup> A historical review by B. Summersbach of pyrophoric alloys will be found in *Chem. Zent.*, 46 (1921), 577.

<sup>2</sup> A good reference for the analytical chemistry of columbium is MOIR, J., *J. Chem. Met. Soc. S. Africa*, 16, 189. A brief outline will be found in JOUNSTONE'S "Rare-earth Industry," p. 60, D. Appleton.

The recrystallization of these salts as double-ethyl sulphates is also practiced, the oxides being converted into the double salts by prolonged agitation with methyl sulphuric acid. In this case absolute alcohol is used as the solvent and the fractionation takes place at 0°C., the resolution of the crystallized portions being performed at 30 to 40°C. In order of increasing solubilities: Tb, Nd, Pr, Ho, Dy. The first three are readily removed from dysprosium, but holmium is not.

Xenotime and gadolinite are the main sources of dysprosium.<sup>1</sup> The closely related elements are erbium, holmium, and thulium.

**Erbium.**—This metal is derived mainly from gadolinite. The generally followed method of extraction is that given on page 1393. The main difficulty is in its separation from europium and gadolinium. Wichers, Hopkins, and Balke<sup>2</sup> say that fractional precipitation of the cobalticyanides or with sodium nitrite gives good results, but that the classic nitrate fusion (fractional decomposition) is best. Willard and James<sup>3</sup> recommend the sodium nitrite method for work on a large scale.

**Europium.**—This metal is obtained from monazite sand residues. It was identified in 1901 by Demarçay, who found he was working with a nitrate more soluble than gadolinium and less soluble than samarium. Its salts are a pale rose color.

The eventual separation is best performed by fractional crystallization of the double-magnesium nitrates, using 30 per cent HNO<sub>3</sub> as the solvent (see p. 1395 for solubilities). The separation of samarium from europium is finally accomplished by adding some bismuth-magnesium nitrate to the solution. The bismuth-magnesium nitrate has a solubility lying between samarium and europium. The bismuth with which each fraction is contaminated is finally thrown out by hydrogen sulphide.

The most closely related elements are gadolinium and terbium.

**Gadolinium.**—This metal was identified in 1880 by C. Marignac in samarskite. It is named for the mineral gadolinite, which, in turn, is named for the Finnish chemist, Johann Gadolin. It is now chiefly obtained from monazite sand residues<sup>4</sup>

Crystallization of alkali-gadolinium sulphate and hydrazine-gadolinium double sulphate give only a rough concentration of gadolinium. Crystallization of the bromates gives a good method for separating the terbium earths from the yttrium group, but does not separate the terbium and cerium groups. The acetate method gives a good separation of Gd from Sa, Pr, and Nd

Compound	H <sub>2</sub> O of crystallization	Grams salt in 100 g. of saturated solution at 25°C.
Lanthanum acetate	1 5	14 47
Praseodymium acetate	1 0	21 48
Neodymium acetate	1 0	20 76
Samarium acetate	3 0	13 05
Gadolinium acetate	4 0	10 37
Yttrium acetate	4 0	8 28

<sup>1</sup> For a general discussion of dysprosium see *J. Am. Chem. Soc.* **39**, 53 and **40**, 591

<sup>2</sup> *J. Am. Chem. Soc.*, **40**, 1615

<sup>3</sup> A critical study of the separation of gadolinium from other metals of the terbium- and ytterbium-earth groups is given in *Z. Anorg. allgem. Chem.*, **100** (1919), 1-30

Double nitrates of bismuth and these earths fractionate in the reverse of the acetates, and alternated with the acetate method, give a good separation. Fractional crystallization of the nitrates gives a rapid separation of the cerium earths in the early stages, but toward the end is much inferior to the acetate. Gadolinium can be rapidly separated from terbium by fractional precipitation with  $\text{NH}_4\text{OH}$ .<sup>1</sup>

Gallium is found chiefly in the flue dusts of zinc works. During the war, when large quantities of zinc were redistilled, residues were left comparatively rich in gallium and indium. This alloy is volatile at the temperature of the ore furnace, but resists distillation for weeks at  $1000^\circ\text{C}$ .

It is probable, according to G. W. Waring, that any practical method of extraction must be founded on fuming the ore at a high temperature, *circa*  $1500^\circ\text{C}$ ., and separating the gallium from the flue-dusts or where redistillation of spelter is carried on, on a tremendous scale. Gallium is interesting because of its low melting point,  $30.8^\circ\text{C}$ ., and high boiling point. It instantly spreads in a thin mirror film over any sort of a dry surface (it wets glass), and it re-collects in a globule when wet with slightly acidulated water. The metal undercools after melting and may not solidify until  $0^\circ\text{C}$ . is almost reached.

Gallium may be separated from iron by the solubility of its hydroxide in  $\text{NaOH}$ , and from aluminum and chromium by precipitation as ferrocyanide. The ferrocyanide ( $\text{Ga}_4[\text{Fe}(\text{CN})_6]_3$ ) when ignited gives  $\text{Ga}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . It is not precipitated by  $\text{H}_2\text{S}$  in acid solution, but is by  $\text{NH}_4\text{OH}$  in  $\text{NH}_4\text{Cl}$  solution. Many of the gallium-aluminum alloys are liquid and wet glass. The metal itself may be produced by electrolysis of the chloride. The potential of the metal is apparently between indium and zinc, but it is distinctly more difficult than zinc to precipitate. It is one of the few elements that expand on solidifying (like bismuth). Its density near the melting point is variously given at from 5.885 to 5.904 as a solid and 6.081 to 6.095 as a liquid. The cubical coefficient of expansion of the liquid is about 0.000055 per degree Centigrade but the metal cannot be used in thermometers, as it wets glass. Its atomic weight is 70.1.

Probably the easiest method of separation of gallium from indium and zinc is by fractional crystallization of the caesium alums.

The metal cannot be separated by electrolysis of sodium hydroxide solutions in the presence of nitrates.

**Germanium.**—Atomic weight, 72.4. The metal can be detected by a modified Marsh test, using  $\text{KOH}$  and  $\text{Al}$ .  $\text{GeH}_4$  is formed, which decomposes at  $340$  to  $360^\circ\text{C}$ . The metal is prepared from germanium-bearing zinc oxides (containing also lead, arsenic, cadmium, indium, tin, and antimony) by treating the oxide with hydrochloric acid and then distilling in a slow current of chlorine gas, driving over  $\text{GeCl}_4$  and  $\text{AsCl}_3$ .  $\text{H}_2\text{S}$  is then passed into the distillate until precipitation is complete. The precipitate is dissolved in hot 50 per cent  $\text{NaOH}$  and  $\text{Cl}_2$  passed in to oxidize the arsenic. Add concentrated  $\text{HCl}$  and continue the  $\text{Cl}_2$ , and distill.  $\text{GeCl}_4$  now comes over between  $90$  and  $100^\circ\text{C}$ . free from arsenic. Collect the  $\text{GeCl}_4$  in water, as hydrated  $\text{GeO}_2$ . The spectroscope shows traces of sodium, calcium, and iron, which can be removed by redistillation. If the mixed sulphides are roasted at not over  $500^\circ\text{C}$ ., most of the arsenic can be removed before distillation, without loss of germanium.

At  $600^\circ\text{C}$ . 30 per cent of the  $\text{GeO}_2$  is lost, at  $800$  to  $900^\circ\text{C}$ ., 80 to 90 per cent is lost.<sup>2</sup> Samarskite, often given as containing germanium, appears to contain none. Ger-

<sup>1</sup> Good general references on gadolinium are *Compt rend*, 149, 127, and *Chem News*, 100, 73

<sup>2</sup> *J Am Chem Soc*, 43 (1921), 2131-2143

manium can also be separated from arsenic as the double fluoride ( $\text{H}_2\text{GeF}_6$ ), which is not affected by  $\text{H}_2\text{S}$ , whereas arsenic is precipitated in HF solution by  $\text{H}_2\text{S}$ .<sup>1</sup>

Urbain describes the preparation from blende as follows: Dissolve the powdered mineral in concentrated  $\text{H}_2\text{SO}_4$  and evaporate to dryness. Dissolve in water and add  $\text{Na}_2\text{S}$ . Treat the residue with 15 per cent  $\text{H}_2\text{SO}_4$ , leaching out the  $\text{ZnS}$ . Treat the insoluble with  $\text{HNO}_3$  and evaporate to dryness. Redissolve in  $\text{H}_2\text{SO}_4$  and from strong acid solution precipitate with  $\text{H}_2\text{S}$ . The precipitate is  $\text{GeS}_2$  with a little As and Mo. Add an excess of  $\text{NH}_4\text{OH}$ , neutralize, and throw out the As and Mo, then precipitate from a strong acid solution.

**Glucium.**—See "Beryllium."

**Hafnium** is of interest in that Bohr predicted the discovery of this element by his theory of the structure of the atom and it was later discovered by X-ray observations by Coster and Hevesy of Copenhagen. Its atomic number is 72. It resembles titanium and zirconium, and it appears to be found only in company with the latter. Dr. Alexander Scott of London claims to have isolated it as a cinnamon-brown oxide from a New Zealand black-sand deposit and ascribes an atomic weight of about 180 to it. It is probably present in the black-sand deposit just below Pablo Beach, Fla.

**Hibernium** is a radio element which is assumed to be the origin of the particles that form the rings between the halves of ytterbium mica. It is probably identical with ytterbium itself.

**Holmium.**—This metal is so like dysprosium that some doubt its elemental character. It is chiefly found in euxenite. It closely resembles didymium, terbium, yttrium, and erbium. The addition of an excess of samarium salt followed by fractional crystallization removes yttrium, europium, and gadolinium. The samarium can then itself be removed as double sulphate (see p. 1393). Fractional hydrolysis of the phthalates increases the holmium content of an holmium-yttrium mixture, as does also fractional precipitation with sodium nitrite, but dysprosium cannot be so separated.<sup>2</sup> Ethyl sulphate crystallization using alcohol as the solvent is also used.

**Indium.**—This is one of the rarest of all the elements. It was discovered by Reich and Richter in 1863, and named by them for the two indigo-blue lines that are characteristic of its spark spectrum. It is found mainly in flue dust from zinc smelters and in metallic zinc.

If metallic zinc is used as the source, the zinc is dissolved in hydrochloric acid, the indium remaining with the lead, undissolved. Indium is precipitated as sulphide in neutral or only faintly acid solution. After freeing from the copper-group metals the iron and indium may be precipitated together by ammonia, the precipitate redissolved in hydrochloric acid, and the nearly neutral solution boiled with an excess of  $\text{NaHSO}_3$ .

Indium precipitates as a basic sulphite. Metallic indium may be prepared by heating the oxide with hydrogen; by electrolysis of chloride or sulphate solution in the presence of pyridine or hydroxylamine. It is a white metal, softer than lead, ductile, and malleable.

It is very like gallium and fractional crystallization of the double-caesium alums is the only effective way of separating gallium and indium. It is stable at ordinary temperatures, but bursts into blue flame on heating.

<sup>1</sup> *Ibid.*, 2540-2552

<sup>2</sup> *Cf Chem Abstr.*, p 2072, of 1918

**Lanthanum** comes down with the double sulphates (p. 1393) and is among the more insoluble of the double-magnesium nitrates. It is said that it can be rapidly separated from praseodymium and neodymium by adding a mixture of 4N  $\text{NH}_3$  and 4N  $\text{NH}_4\text{Cl}$ , a drop at a time, at 50°C., using mechanical stirring, but this is a laboratory rather than a commercial method. Fractional precipitation with ammonia in the presence of zinc and ammonium nitrates is also recommended. Its atomic weight was redetermined in 1921 as 138.91.

**Lutecium.**—In 1907, when G. Urbain was examining supposedly pure ytterbium nitrate fractions he obtained different spectroscopic lines for the various portions. He decided that ytterbium was, therefore, composed of lutecium ( $\text{Lu} = 174$ ) and neoytterbium, 170. The reactions are essentially the same for neoytterbium and lutecium.<sup>1</sup> In 1916, an atomic weight of 175 was assigned to lutecium.<sup>2</sup> It is named from the ancient Roman name for Paris, Lutetia.

**Molybdenum.**—The methods ordinarily given for the treatment of wulfenite (the most common mineral) are to leach with  $\text{Na}_2\text{S}$ , the molybdenum going into solution as  $\text{Na}_2\text{MoO}_4$ , or to fuse with soda ash, sodium hydroxide, and powdered coal, obtaining a lead bullion and a slag from which sodium molybdate may be leached. In either case, the molybdenum is recovered from this solution by precipitation as  $\text{CaMoO}_4$ .

For ferromolybdenum production, the finely ground pulp is mixed with soda-ash solution and heated to boiling, and the molybdenum thrown from the filtered solution by  $\text{Fe}_2(\text{SO}_4)_3$  or  $\text{FeCl}_3$  and the precipitate smelted with carbon in an electric furnace.

Molybdenum sulphide is said to be acted on at above 268°C. by chlorine, and it is suggested that pure sulphides could be treated with chlorine and  $\text{MoCl}_4$  condensed.

Molybdenum has a density of 10.2; tensile strength, 260,000 lb. per square inch; melting point, 2550°C.; boiling point, 3617°C.; specific heat, 0.072 cal. per degree centigrade; linear coefficient of expansion,  $5.15 \times 10^{-6}$ ; thermal conductivity, 0.346 cal. per degree per cubic centimeter; electrical resistance, microhms per cubic centimeter at 15°C., annealed, 4.8 (all according to Balke). See also p. 1336.

**Nebulium** is a hypothetical element of atomic weight 1.31.<sup>3</sup> It is not known terrestrially.

**Neodymium.**—This is found chiefly in cerite, which may be dissolved in acids, and the earths precipitated as oxalates, which are converted into oxides on ignition. These oxides are then treated with nitric acid, which on heating produces basic ceric salts. Lanthanum, praseodymium, neodymium, samarium and ytterbium are in solution. Crystallization of the nitrates from nitric acid tends to concentrate lanthanum, cerium, neodymium, and praseodymium in the mother liquors. Crystallization of the double-magnesium nitrates tends to throw lanthanum and neodymium into the crystals.

**Neothulium.**—See Aldebaranum.

**Neoytterbium.**—In 1908, Urbain announced that he had fractionated ytterbium compounds by a long series of crystallizations into two distinct compounds, the base of one with an atomic weight of 170 (neoytterbium) and the other with an atomic weight of 174 (lutecium). The name neoytterbium has been dropped and that of ytterbium given to this fraction, the unseparated earth often being spoken of as "the old ytterbium."

<sup>1</sup> *Comp rend* 143, 750 Cf Neoytterbium and Ytterbium, this book

<sup>2</sup> See *Compt rend*, 149, 127, and *Chem News*, 100, 73

<sup>3</sup> NICHOLSON, J W, *Roy Astron Soc M N*, 70, 349

**Niobium.**—See Columbium, which is the proper name.

**Praseodymium** comes out in the insoluble double alkali sulphate fraction and then among the less soluble double-magnesium nitrates, (see scheme, p. 1394). Its name means "the green twin." It can be prepared by electrolysis of the anhydrous chloride. It is a silvery white, easily tarnished metal, of specific gravity 6.6, which melts at 940°C. and kindles in air at 290°C.

**Rubidium** was discovered in 1861 by Bunsen and Kirchhoff, in lepidolite, and named for two dark red lines. It may be recovered from lepidolite by decomposition with sulphuric and hydrofluoric acid; or from any silicate by decomposing with  $\text{CaCl}_2$  and  $\text{NH}_4\text{Cl}$  and heat. From the first, caesium-rubidium alum can be recovered. From the second, after precipitation of  $\text{CaSO}_4$  with  $\text{H}_2\text{SO}_4$ , and  $\text{CaCO}_3$  with  $(\text{NH}_4)_2\text{CO}_3$ , the addition of platinic chloride will throw down caesium-rubidium chlorplatinate.

Rubidium metal may be prepared by electrolysis of the fused chloride. It is a soft silvery metal. It melts at 38.5°C. and boils at 696°C. It takes fire spontaneously in air and decomposes water vigorously.

Caesium and rubidium are themselves separated by fractional crystallizations of caesium-iron and rubidium-iron alums, followed by removal of the iron.

**Samarium.**—Material containing samarium is purified as follows:<sup>1</sup> Cerium is thrown out by bromine and marble; La, Pr, and Nd by fractionation of the double magnesium-nitrates; Eu and Gd by fractionation of the magnesium double nitrates along with the double nitrate of Bi and Mg; and finally the Sm is alternately precipitated as  $\text{Sm}(\text{OH})_3$  and  $\text{Sm}_2(\text{C}_2\text{O}_4)_3$  and recrystallized as hydrated chloride. The bismuth-magnesium nitrate is added and has a solubility intermediate to samarium and europium, so that it thus affords a separation. The last of the bismuth can itself be removed by  $\text{H}_2\text{S}$ . The metal is supposed to melt about 1300°C. It is named for samarskite, in which mineral it was first discovered.

**Scandium.**—Scandium is chiefly found in the wolframite of Zinnwald, although Nilson discovered it in 1879 in euxenite.

Scandium can be separated from wolframite residues by dissolving the oxides in hydrochloric acid and precipitating with ammonium fluoride.<sup>2</sup> To separate pure scandium salt from this precipitate, lead, copper, etc. are precipitated with hydrogen sulphide from acid solution of scandium chloride; iron and manganese from solutions of scandium-potassium carbonate, the former with potassium-hydrogen sulphide, the latter with iodine in potassium iodide solution; molybdenum is removed as sulphide by precipitation in the presence of formic acid; and the thorium, yttrium, and ytterbium by precipitation of scandium-sodium carbonate, combined with the fractional crystallization of sodium formate.

The scandium is then thrown out of its solutions by  $\text{HF}$  or  $\text{H}_2\text{SiF}_6$  or  $\text{Na}_2\text{SiF}_6$  in acid solution, after which it will only contain small amounts of thoria, yttria and ytterbia. It can be further purified by precipitation with  $\text{Na}_2\text{S}_2\text{O}_8$ , but will probably still contain about 1 per cent. of thoria.

The  $(\text{NH}_4)_2\text{ScF}_6$ , precipitated by addition of ammonium fluoride to scandium salts, also can be used for fractionating. This salt hydrolyzes to  $(\text{NH}_4)_2\text{ScF}_6$  and  $\text{NH}_4\text{ScF}_4$ .

Pure scandium is diamagnetic. Yttrium and cerium are the closest related elements. The atomic weight is now ordinarily given at 45.1.

<sup>1</sup> OWENS, BAKER, and KREMERS, *J. Am. Chem. Soc.*, 42 (1920), 515.

<sup>2</sup> STERN, J., *Z. Elektrochem.* (1914), 289



M. Speter says scandium can be separated directly by decomposing its minerals by acid, or fusing them with alkali and dissolving the melt in acid. The acid solution is filtered, the rare earths precipitated as oxalates and boiled with  $H_2PO_4$ , filtered again, the precipitate taken up in sulphuric acid and reprecipitated as oxalate.<sup>1</sup>

Scandium is one of the three elements clearly forecast by Mendeleef. His "ekaluminum" is gallium, "ekasilicum" is germanium, and "ekaboron" is scandium.

**Selenium.**—This element was discovered in the dust collected in acid-chamber flues by Berzelius in 1817. It is widely distributed in the ores of lead, copper, gold, and silver and in pyrites. The chief source of the commercial metal is the flue dust from plants treating electrolytic copper slimes. There are a number of allotropic forms. From the metallurgical standpoint only three varieties are important: the finely divided material produced by precipitating selenium from chloride solutions with sulphur dioxide or carbon monoxide (the former being the common commercial precipitant); vitreous selenium; and metallic selenium. If the first form, which is a bright-red to dark-brown precipitate (this precipitated modification itself runs through several allotropic forms), is heated it melts to a black mass, which, when cooled quickly gives a black to purple-black vitreous bar when viewed by reflected light and a beautiful red if drawn while hot into thin sheets. When the vitreous modification is kept for some time at a temperature of 150°F. or over it changes to a silvery-gray modification (metallic selenium), which is unique among metals in having its electric conductivity greatly altered by changes in the intensity of the light with which it is illuminated.

The resistance falls with increased illumination and increases as the temperature increases.

The change from the vitreous to the metallic state is strongly exothermic and becomes more rapid as the temperature increases up to about 210°F. The metal melts at 217°C.

The metallic modification can be changed back to the vitreous by melting and quick cooling.

When ores are smelted for copper, selenium and tellurium enter the matte and remain largely in the blister copper. A large proportion remains in the copper when blister is refined to anode copper and the two are quantitatively slimed in the electrolytic tank room.

In the slimes-treating furnace selenium volatilizes largely, particularly if there is a little free sulphuric acid in the slime and slow roasting. Tellurium has a much greater tendency to enter the furnace slags but even tellurium is to some extent volatilized. In the flues the tellurium condenses before the selenium does, so that in analyzing chamber residues, there is a constant increase in the ratio of selenium to tellurium at increasing distances from the furnace.

Much of the selenium in these dusts exists as  $SeO_2$  and is directly soluble in water. The remainder is taken into solution by leaching with sodium chlorate and hydrochloric acid (a process introduced by Liddell in 1907). Some tellurium will also be dissolved, but if sufficient hydrochloric acid be added to the solution to bring it up to 50 per cent hydrochloric acid (as compared with the concentrated aqueous solution) selenium will be precipitated by the passage of  $SO_2$  and tellurium will not be. After the solution is decanted from the precipitated selenium, if it be diluted with water and allowed to stand for some time the tellurium will come down as a black precipitate.

<sup>1</sup> German patent 282657, 1911.

The selenium precipitate is washed and dried, then either powdered, or melted in enamel-ware pans and cast.

The leaching operation is most conveniently carried on in stoneware tanks, the precipitation either in stoneware jars, or, even better, in barrels painted with P. & B. paint. The precipitation should not be carried on too fast or the precipitate will occlude sulphuric acid, which oxidizes the metal during drying and melting; nor should the precipitation be from too concentrated a solution or a purplish-black modification will result which is very hard to dry and very difficult to melt.

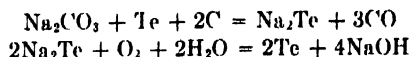
The compounds of selenium are analogous to those of sulphur. The hydride ( $\text{H}_2\text{Se}$ ) is worse smelling than the sulphur compound and more poisonous. A bubble of the pure gas is said to have paralyzed for six months the olfactory nerves of its discoverer.

It forms  $\text{SeF}_2$  (soluble in  $\text{HF}$ , hydrolyzed by  $\text{H}_2\text{O}$ );  $\text{Se}_2\text{Cl}_2$ ,  $\text{SeCl}_4$ ,  $\text{Se}_2\text{Br}_2$ ,  $\text{SeBr}_4$ ,  $\text{Se}_2\text{I}_2$ ,  $\text{SeI}_4$ , and various complex chlorbromides and oxyhalides.

It forms  $\text{SeO}_2$  and  $\text{SeO}_3$ , which are the anhydrides of corresponding acids. Selenic acid is unaffected by  $\text{SO}_2$  or  $\text{H}_2\text{S}$  (differs from selenious acid in these particulars), but is slowly reduced by boiling concentrated hydrochloric acid. Barium selenate is completely decomposed by hydrochloric acid, as is also the tellurate, thereby differing from barium sulphate.

Reactions of importance from the metallurgical standpoint, in addition to those given above, are: the amorphous-powder modifications are soluble in potassium cyanide, forming  $\text{KCNSe}$ . Tellurium is insoluble (this gives a method of separation). Those amorphous modifications precipitated at low temperatures are soluble in carbon disulphide, but those precipitated at or heated to high temperatures are not soluble, nor is tellurium. Both selenium and tellurium go into colloidal dispersion when heated with strong sulphuric acid, the beautiful purple produced by tellurium being a characteristic test for it. The metals again precipitate on cooling or dilution. If, however, the heating is carried on long enough the metal is oxidized, forms sulphates, and is no longer reprecipitated on cooling or dilution.

Both selenium and tellurium and their compounds when heated with an alkaline carbonate and carbon form alkaline selenides and tellurides which are decomposed by the passage of air through their solutions. This is the process introduced by A. E. Knorr for the recovery of tellurium from high-tellurium flue dusts.



Metallic selenium has a specific gravity of 4.8 and melts at  $217^\circ\text{C}$ . The specific gravity of the vitreous modification is 4.28 and of the amorphous about 4.26. A red crystalline modification has a specific gravity of 4.47 and seems to melt between  $170$  and  $180^\circ\text{F}$ ., but passes over quickly to the metallic modification and solidifies, giving out 55 cal. per gram. Selenium boils at  $680^\circ\text{F}$ . at 700 mm., at about  $310^\circ\text{F}$ . at low pressures. It burns in air with a blue flame, forming  $\text{SeO}_2$ , but the reaction requires external heat to maintain it. Above  $250^\circ\text{F}$ . it unites with hydrogen, more quickly as the temperature is raised.

The chief use of selenium in tonnage is as a coloring matter for ruby glass. It is also used in electrical devices such as automatic light controls, etc., where its varying conductivity under varying illumination is of use, but the weight used in a selenium cell is almost negligible.<sup>1</sup>

**Tantalum.**<sup>1</sup>—The metal is usually prepared from tantalite, the most important of the tantalum minerals. The finely pulverized tantalite is fused with potassium hydroxide, converting the tantalum and columbium to soluble tantalates and columbates. The melt is then dissolved in water and after filtration the solution is neutralized with hydrofluoric acid, converting the columbium and tantalum into double fluorides with potassium. (Sodium cannot be used.) The potassium-tantalum fluoride then precipitates and can be purified to any desirable extent by recrystallization. The metal is produced by reduction of the oxides *in vacuo*, the oxide being obtained by igniting tantalic acid, precipitated from the double fluoride. Aluminum will reduce it (thermit reaction).

Tantalum is not attacked by *aqua regia* or nitric or hydrochloric acid, either hot or cold. Solutions of caustic alkalies do not attack it. It is slowly attacked by boiling concentrated sulphuric acid and by hydrofluoric acid. It is rapidly attacked by a mixture of nitric and hydrofluoric acids. When tantalum is heated in air the surface becomes blue at about 400°C. and at a somewhat higher temperature, nearly black. Above a dull-red heat the white oxide is produced and the metal gradually burns. The metal combines readily at elevated temperatures with hydrogen, nitrogen, and chlorine (the last producing the volatile pentachloride). The metal is tough and highly ductile and malleable.

As an electrode the metal is of interest. Gold or platinum may be deposited on tantalum and removed with *aqua regia*. If two plates of bright tantalum are immersed in an electrolyte and a direct current passed, film forms on one plate in a few seconds and the voltage drops. With sulphuric acid of the strength ordinarily used for electric storage batteries, the current is less than 1 milliamp. with a voltage up to 75.

If a tantalum and a lead plate are placed in an electrolyte and an alternating current passed, the current in one direction is shut off and a pulsating direct current obtained. Hydrogen gas is given off at the tantalum plate.

Tantalum has a density of 16.6; atomic volume of 10.9; tensile strength, small wires, 130,000 lb. per square inch; compressibility per kilogram per square centimeter,  $0.50 \times 10^{-6}$ ; Young's modulus of elasticity, 19,000 kg. per square millimeter; melting point, 2850°C. (?); specific heat, 0.0365; linear coefficient of expansion per degree Centigrade,  $7.9 \times 10^{-6}$ ; thermal conductivity, calories per cubic centimeter per degree Centigrade, 1.30; electrical resistance (annealed), microhms per cubic centimeter at 15°C., 14.6; electrical coefficient of resistance, 0.00335 per degree Centigrade. Discovered in 1802 by Ekeberg; named for "Tantalus."

**Tellurium.**—The presence of this element was suspected by Mueller von Reichenstein in 1782 in a sample of gold ore from Austria, and was isolated in 1798 by Klaproth. It is of common occurrence as sylvanite (gold telluride), particularly in Colorado.

The metallurgy is intimately connected with that of selenium and reference should be made to what has been said on that metal (pp. 1404 to 1405).

Tellurium is a silver-white metal, atomic weight, 127.5; melting point, 452°C.; boiling point, 1390°C. (760-mm. pressure); density, 6.2; tensile strength, 115 kg. per square centimeter.

It is used as a crystal detector in radio work, as a coloring matter in glass and ceramic trades, and, in the form of diethyl telluride, is an antiknock compound in the internal-combustion engine.

It unites readily with chlorine, forming  $\text{TeCl}_2$  and  $\text{TeCl}_4$ , and with oxygen, forming  $\text{TeO}_2$  and  $\text{TeO}_3$ , which form acids  $\text{H}_2\text{TeO}_3$  and  $\text{H}_2\text{TeO}_4$ , analogous to sulphurous and sulphuric, except tellurous acid is more stable and telluric acid less so than the sulphur analogs.

It is a brittle crystalline-structured metal, tarnishing slowly in air, but less so than lead. Its compound with hydrogen,  $\text{H}_2\text{Te}$ , has a frightful odor. It is peculiar in that it is eliminated almost entirely from the body as methyl telluride, via the lungs, giving a garlic odor to the breath.

Tellurium combines readily with many metals when heated. The telluride of aluminum can be formed by dropping tellurium into molten aluminum. This telluride is an interesting substance, decomposing with water to give aluminum hydroxide and hydrogen telluride, which is highly poisonous and almost intolerably offensive.

Magnesium telluride is similarly formed, with explosive violence. In general, in making selenides and tellurides by addition, a mask and goggles should be worn.

**Terbium**, found chiefly in gadolinite, belongs to the Sm-Nd-Gd-Pr group. The main difficulty is to free it from holmium and dysprosium. Its bromate is more soluble than theirs, its nitrate and chloride less so. Its name is derived from "Ytterby," near which town gadolinite was first found. Terbium oxide is black<sup>1</sup>. Crookes original element "ionium," not the radium decomposition product, seems to have been terbium.

**Thallium** is chiefly found in acid-plant flue dust, its extraction depending on the solubility of the sulphate and sparing solubility of the chloride. The flue dust is boiled with dilute  $\text{H}_2\text{SO}_4$  in wood or earthenware containers, filtered and HCl added. The precipitate is dissolved in  $\text{H}_2\text{SO}_4$  and thallium again thrown down. Salt can be used instead of HCl. The metal can be obtained by fusing the chloride cautiously with KCN and  $\text{Na}_2\text{CO}_3$ , or it can be reduced by zinc and melted in an inert gas, but A. Kolliker<sup>2</sup> says the metal on washing quickly oxidizes and then dissolves, affording an easy separation from other metals. The metal is highly toxic, probably ranking next to mercury among the elements. The metal melts about  $301^\circ\text{C}$ . While most authorities say that  $\text{Tl}_2\text{O}_3$  dissolves readily in HCl, this seems very doubtful.

Thallium is one of the few metals whose lower oxide is more stable than the upper. Its binary alloys with lead have a decidedly higher melting point than has either constituent, indicating possibilities in their use as insoluble anodes<sup>3</sup> and for acid-chamber linings. Lead-thallium and lead-thallium-tin alloys also have theoretical possibilities as high-temperature solders.

**Thorium**.—Atomic weight, 232.15; melting point about  $1800^\circ\text{C}$ . The principal commercial mineral carrying thorium is monazite, although small quantities of thorianite and thortite have been used commercially. These latter minerals, however, are limited in quantity. Monazite is composed mainly of phosphates of the cerium and lanthanum earths together with a variable percentage of thorium. Its specific gravity is from 4.8 to 5.5, and its color varies from yellow-gold to reddish brown and is occasionally even dark brown or black. Monazite occurs in certain gneissic and granitic rocks, but the actual commercial deposits

<sup>1</sup> For a general resumé of the work on terbium see articles by URBAIN, G., *Chem. News*, 100, 73; *Chem. Ztg.*, 38, 745

<sup>2</sup> *Chem. Ztg.*, 43, 231

<sup>3</sup> An alloy experimented with by Dr. Colin G. Fink and highly resistant in acid sulphate solutions containing both  $\text{HNO}_3$  and HCl was Pb, 70, Sn, 20, Tl, 10 per cent

which are worked are alluvial. The principal sources are Brazil and India, although the mineral has been mined successfully in the United States, in the Carolinas, Idaho, and Florida. It has been found in Switzerland, Africa, and Australia, and to a limited extent in river rocks and placers in Ekaterinburg, Russia.

Monazite is usually found in gravels of small streams and in bottom lands. In Brazil and India it occurs mainly in the beach sands of sea water. It is found in small crystals in gneiss, granite, and pegmatite rocks. As these rocks become disintegrated the crystals are washed into the creeks and streams and, together with other heavy sands, are deposited in the beds of water courses. On the coast of Brazil the monazite from the crystalline rocks of the coast mountains is concentrated in the sea sands by the waves of the sea. The bulk of the monazite in Brazil is found in the states of Espirito Santo and Bahia. In India, the main location is in the Travancore district in southern India. The deposits of the Carolinas in the United States cover an area of several hundred square miles east of the Blue Ridge Mountains. Practically all of the monazite mined in the Carolinas is derived from the gravel in the streams and bottom lands, the miners usually following the course of the streams and creeks. The gravels vary greatly in thickness; in general, they are between  $1\frac{1}{2}$  and  $2\frac{1}{2}$  ft. thick. Monazite is also found in Florida.

**Extraction from the Ores.**—The methods of treating monazite for the production of thorium nitrate are more or less secret and are changed from time to time, depending upon conditions, costs of chemicals, etc. The general principles of the commoner method used before the war are as follows: The mineral is heated in cast-iron pans or pots with about twice its weight of concentrated sulphuric acid, until the monazite is completely decomposed, giving a white mass of sulphates, which are largely insoluble in the acid. This mixture is run into cold water in a lead-lined vat and the whole stirred until solution is complete. The material is allowed to stand for a considerable period in order that the insoluble matter, consisting of silica, zircon, rutile, and other minerals insoluble in concentrated sulphuric acid, may settle out, and the solution which contains the rare earths, phosphates, etc. is decanted off. If now the free acid is partially neutralized so as to reduce the acidity, thorium phosphate is precipitated first, because it is less soluble than the phosphates of the other rare earths. The thorium phosphate still carrying quantities of other rare-earth phosphates is filtered, dissolved in a minimum amount of acid, and the fractional precipitation repeated.

One method of still further purifying the precipitate is to boil it with oxalic acid,<sup>1</sup> which causes the thorium to be precipitated as thorium oxalate, while the phosphoric acid remains in solution. The precipitated oxalates are digested for a prolonged period with sodium hydroxide and the hydroxides formed are dissolved in hydrochloric acid. If the acid solution is then carefully treated with sodium hydroxide, until about one-sixth of the bases have been precipitated, thorium hydroxide will be precipitated before the other hydroxides. Baskerville has suggested the volatilization of the phosphoric acid by mixing 1 part of monazite with 1.1 parts of petroleum coke, 0.8 parts of lime, and 0.15 parts of fluorspar, and heating in an electric furnace. This not only removes the phosphorus but also gives the latter in a marketable form. Further purification of the thorium hydroxide may be carried on in one of several ways. The oxalate method depends upon the fact that thorium oxalate forms a

<sup>1</sup> *J. Phys. Chem.*, **20** (1916), 640.

double salt with ammonium oxalate, which is soluble, while cerium oxalate is almost insoluble. The carbonate method is based upon the fact that thorium carbonate forms double salts with the alkali carbonates, which are soluble, whereas the double salts of the cerium earth oxalates are insoluble. The sulphate method depends upon the fact that certain hydrated sulphates of thorium possess a considerable difference in solubility from the sulphates of the cerium earths. This fact is used as a basis for fractional crystallization. Whichever method is used, after the thorium is sufficiently purified it is converted into thorium carbonate or hydroxide and dissolved in nitric acid and the solution evaporated until thorium nitrate ( $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ ) crystallizes out. After the beginning of the war, owing to the greatly increased cost of certain chemicals, especially oxalic acid, considerable modifications were necessary in the process used for treating monazite sand. These changes in practice have been kept secret, but consist essentially in combinations of the methods described above.

In a recent patent<sup>1</sup> the following method is described. The crude thorium phosphate is boiled with caustic and then dissolved in sulphuric acid. Thorium fluoride is precipitated by hydrofluoric acid and dissolved in sodium bicarbonate. Thorium hydrate is precipitated by caustic soda, converted to sulphate, and crystallized. The sulphate crystals are converted to hydrate with ammonia and the cycle repeated. The thorium is finally converted to the nitrate.

The element mesothorium, a radioactive product of thorium and hence a constituent of all thorium minerals, deserves mention, since it is now being recovered as a by-product in the refining of monazite.<sup>2</sup> Barium chloride (0.2 per cent of the weight of ore) is added to the ore, and then sulphuric acid. After dilution, the slimes containing the mesothorium and barium sulphate are decanted from the coarse residue, settled or filtered out of the solution, and treated for the further concentration and recovery of the mesothorium.

**Concentration Methods.**—The first stage of concentration in the Carolinas involves the use of oscillating tables or sluice boxes. The concentrates produced in the sluice boxes contain 20 to 60 per cent monazite. The crude concentrates must be further refined, and are best treated by electromagnetic separators, of which the Wetherill type has proved to be the most successful.<sup>3</sup> The separation of the minerals is dependent upon the difference in their magnetic permeability. The magnets are best adjusted so that the first pole of the first magnet removes from the sand the highly magnetic material, as, for instance, the magnetite and ilsemanite; the second pole of the first magnet extracts the garnets and also the finer grains of the ilsemanite; the third magnet (being the first pole of the second magnet) removes all of the coarser grains of the monazite; and the last pole extracts the finer grains of the monazite. At the end turn of the rubber belt of the machine, the residues are dropped into a receptacle.<sup>4</sup> The grade of the concentrates obtained from the different large sources of supply varies considerably. The average concentrate obtained in the Carolinas was about  $3\frac{1}{2}$  to 4 per cent thorium oxide, whereas that obtained from Brazil averages around 6 per cent. It was for this reason very largely that the industry in the Carolinas was ultimately given up. The monazite from India has even a higher grade than that from Brazil, averaging around 9 per cent thorium oxide, and some of it going still higher. As concentrate of this type carries about 27 per cent cerium

<sup>1</sup> British patent 179399

<sup>2</sup> Department of Interior, U S Bureau Mines, *Tech. Paper* 265

<sup>3</sup> GUNTHER, "Electromagnetic Ore Separation," 1909

<sup>4</sup> KIRKILL, K L U S Bur Mines, *Tech. Paper*, 110.

oxide, 29 per cent lanthanum and allied oxides, and 2 to 4 per cent yttria and allied oxides. It also contains about 26 per cent phosphoric acid.

**Metallic Thorium.**—The metal has probably not yet been prepared in a perfectly pure state. Reduction of the oxide with magnesium is never complete, and attempts to reduce with carbon give a mixture of the metal and carbide. Moissan and Honigschmid heated the purified anhydrous chloride with sodium in a sealed glass tube and obtained a product which was said to contain only 3 per cent of the oxide. The amorphous metal is a dark-gray powder of specific gravity 11.3 and when hammered and strongly heated it has a density of 12.16. It burns readily in air, and melts at about 1700°C., although the pure metal would probably melt at a higher temperature.

**Uses of Thorium.**—The main use of thorium is in the incandescent gas-mantle industry. The successful use of incandescent gas mantles began in 1893 when Welsbach patented the use of a mixture containing 98 to 99 per cent thorium oxide with 1 to 2 per cent cerium oxide (English patent 124, of 1893). With this mixture the oxides give a brilliant light and have a maximum illuminating power. The cerium oxide is probably in solid solution in the thorium oxide.<sup>1</sup> Thorium oxide is a very poor heat conductor and hence can be raised to a high temperature. The small amount of cerium oxide gives enough color for efficient light emission. An outline of the methods used for obtaining mantles is as follows: The mantle itself is made either of ramie fiber or of artificial silk. The woven mantles are thoroughly washed in a 2 per cent solution of nitric acid, distilled water, and then in dilute ammonia. The latter is thoroughly washed out by distilled water. The mantle is dried in a current of hot air and then dipped in a solution of thorium and cerium nitrates, consisting of 99 per cent thorium salt and 1 per cent of cerium.

Small quantities of beryllium or magnesium nitrate are added for strengthening purposes. The upright mantles are then fitted with an asbestos loop by which they are suspended, whereas the inverted mantles are fixed to a supporting ring. Those portions on which there is especial strain are sometimes treated with a thorium solution containing much larger proportions of calcium, aluminum, or magnesium salts. The mantle is then shaped and burnt off from the top downward by applying a Bunsen flame. During this process of burning off, there is considerable shrinkage. As soon as the carbonization is finished, the mantle is shaped and heated with low-pressure burners, after which it is hardened by heating in a high-pressure burner. The mantles, now consisting of nothing but the ash skeleton, are immersed in a collodion solution containing collodion, ether, camphor, and castor oil. The ingredients may vary to some extent. After drying at a moderate temperature, they are ready for use.

**Thulium.**—Thulium was discovered in 1879 by Cleve, when he was attempting to find out what gave the rose color to the salts of "old erbium." He named it for "Thule," an old name for Scandinavia. Is among the most soluble of the double nitrates. (See scheme on p. 1394 for its separation.) In solution with cerium and yttrium only it is completely separated from them by precipitation with  $\text{H}_2\text{SiF}_6$ .

**Titanium.**—The chief commercial source of titanium is ilmenite, from which it is recovered by dissolving in concentrated sulphuric acid and then adding sodium chloride to the concentrated solution to throw down sodium-titanium sulphate.

Alkaline hydroxides or carbonates precipitate titanium hydroxide from solution, a bulky gelatinous precipitate. The metal can be produced from the oxide by the thermit reaction.

<sup>1</sup> WHITE AND TRAVERS, *J. Soc. Chem. Ind.*, **21**, (1902), 1012

The Cartegat-Devaux process for the production of the metal is to reduce ore at red heat with coal, then to heat the reduced mass with chlorine gas at gradually increasing temperatures, distilling off successively iron, silicon, and titanium.

In the preparation of pure titanium from the chloride Maurice Billy recommends sodium hydride for the precipitant.<sup>1</sup>

$\text{TiCl}_4 + 4\text{NaH} = \text{Ti} + 4\text{NaCl} + 2\text{H}_2$ . The purified oxide can also be reduced by heating in a current of hydrogen gas.

Billy states that by reducing titanium dioxide with titanium it is possible to obtain the following:

Between 700–800°C., a blue oxide,  $\text{Ti}_2\text{O}_3$ .

Between 900–1000°C., a violet oxide,  $\text{Ti}_2\text{O}_3$ .

Between 1100–1200°C., a black oxide,  $\text{Ti}_2\text{O}_3$ .

Between 1400–1500°C., a brown oxide,  $\text{TiO}$ .

Titanium tetrachloride is the most important of the smoke-screen compounds, through its hydrolysis with the water vapor of the air.

Titanium is important as an alloy metal for permanent magnets, using 15 to 30 per cent Ti, 1 to 5 per cent Mn, 0.6 to 1.2 per cent C, with or without 2 to 5 per cent of Cr. Steels containing 10 to 30 per cent Cr, 5 to 12 per cent Ti, and 3 to 5 per cent Mo are said to be highly resistant to corrosion.

Titanium is brittle when cold, but can be forged at red heat. So far it has proved impossible to draw it into wire. It is interesting in that in the iron blast furnace titaniferous ores give copper-colored cubes of  $\text{Ti}(\text{CN})_2 \cdot 3\text{Ti}_2\text{N}_2$  in the slag.

**Victorium.**—A metal reported by Crookes, apparently gadolinium.

**Yttrium.**—This metal forms a soluble double-alkali sulphate and is among the more soluble double nitrates (cf. pp. 1394 and 1395). Probably the best separation from the other members of the yttrium group (Dy, Ho, Er, Tm, Yb, and Lu) is the classic "fused-nitrate" method (see p. 1395), but fractional precipitation as the cobalticyanide or as the nitrite (using  $\text{K}_3\text{Co}(\text{CN})_6$  for the precipitant with the first and  $\text{NaNO}_2$  for second) gives fair separations. The Yt remains in solution. Fractional precipitation with potassium chromate does not remove erbium or holmium; the nitrite does. Yttrium mixed metal can be produced by decomposing the anhydrous chlorides *in vacuo* with sodium or by electrolysis of the mixed chlorides. It is a blue-gray color and disintegrates in time to powder, especially if exposed to moist air. The element derives its name from the Swedish town of Ytterby. Atomic weight, 89.33; melting point, about 1490°C.

The acetate is apparently a hydrophilic colloid.<sup>2</sup> It is soluble in water in all proportions, can be salted from its aqueous solutions like soap, and when shaken the solution lathers quite freely. Evaporation of the solution causes no crystallization, but results in an amorphous mass resembling gelatin. Solution of the residue from this evaporation takes place very much after the manner of the solution of gelatin, with first a swelling and softening and then a gradual dissemination of this gel through the liquid. It is in the exploitation of these peculiar properties of the zirconium compounds that the most important industrial applications may yet be found. The hydroxide is a strongly adsorptive compound.

Salts of the metal hydrolyze strongly, and Rodd<sup>3</sup> says no normal salt exists in aqueous solution. Also the extent of the hydrolysis seems to depend on the method by which the salt was prepared.



Zirconium is precipitated from its weakly acid solutions by sodium thiosulphate. The phosphate precipitates in strong mineral acid solutions, but the precipitate is difficult to wash and can only be broken up by fusion with caustic soda.

For extracting  $ZrO_2$  from the ores Marden and Rich say that for commercial extraction the best method is to heat 1 part of ore with 4 parts of concentrated sulphuric acid until fumes have ceased and then raise the temperature to  $650^\circ C$ . After cooling, extract with 50 parts of cold water and filter, then add sodium carbonate until  $Zr(OH)_4$  just begins to form. Allow the solution to stand three or four days, during which  $4ZrO_2 \cdot 3SO_2 \cdot 14H_2O$  will gradually settle out. This is ignited to give  $ZrO_2$ .<sup>1</sup>

Another method recommended for the treatment of zirkite is to sift 100-mesh material into a fused mass of 3 parts sodium carbonate and 3 parts sodium hydroxide. Fuse for 1 hr., cool, crush, and leach with hot water. The washed residue is then digested with 1:1 HCl and the solution filtered. Neutralize with soda ash as far as can be done without precipitation and pass  $SO_2$  into the hot solution.

Zirconium melts about  $2800^\circ C$ ., above Mo and close to Ta.<sup>2</sup> The melting point of the oxide is given anywhere from 2560 to over  $3000^\circ C$ . If the metal actually melts at  $2800^\circ C$ ., the higher value for the melting point of the oxide would seem correct.

Zirconium can be produced by the reduction of  $ZrCl_4$  with metallic sodium. It melts at about  $2800^\circ C$ . and alloys well with Ni, Cu, Au, Al, Mg, and W. The oxide  $ZrO_2$  becomes practically insoluble on strong ignition in every acid except hydrofluoric, and doubtless the conflicting statements as to solubility merely reflect differences in ignition temperatures. The specific gravity of the metal is about 6.4.

Bruère and Chauvenet say there is but one nitride ( $Zr_3N_4$ ). In reducing atmosphere, the oxide has a strong tendency to form carbides.

It is said that a pure  $ZrO_2$  can be obtained by heating zircon with  $1\frac{1}{9}$  times its weight of carbon to whiteness, then treating with dilute sulphuric acid and filtering.  $Zr(SO_4)_2$  is in solution.

A. J. Phillips<sup>3</sup> says the best way to produce  $ZrCl_4$  is to bubble  $Cl_2$  through hot water and then pass the moist gas through a retort heated to about  $500^\circ C$ . and filled with small balls of zirconia and petroleum coke. The following table of chlorination temperatures is given.

CHLORINATION BY MIXTURES OF  $Cl_2$  AND CO

	CO in excess	$Cl_2$ in excess
$ZrO_2$ .....	480	425
$SnO_2$ .....	400	
$MgO$ .....	475	
$Al_2O_3$ .....	450	
$Fe_2O_3$ .....	460	370
$Cr_2O_3$ .....	625	
$MnO_2$ .....	460	
$U_3O_8$ .....	500	

**Treatment of Platinum Concentrates.**—In general, the recovery of the platinum-group metals is based on their solution in *aqua regia* and their recovery as double-ammonium chlorides.

In the treatment of crude platinum concentrates, the first step is a 24-hr. leaching with 3 l. of 20°Bé. hydrochloric acid and 1 l. of 35°Bé. nitric acid per kilogram of platiniferous material, keeping the mass (held in porcelain vessels) at 80°C. The insoluble residues from several portions thus treated will ordinarily be combined and treated again in the same manner for the recovery of further platinum. The insoluble residue from this retreatment is eventually treated for the recovery of iridium and osmium (see pp. 1414–1416).

The solution is decanted from the insoluble residue and evaporated with the addition of about 1 l. of hydrochloric acid to each 6 or 7 l. of first solution. The evaporation should be carried to 140 or 150°C., in order to alter the iridium to such a form that it will not precipitate with the platinum in the next step.

Redissolve the evaporated mass in hot water and allow to stand for a few hours. Usually a residue of gold and platinum will separate out. This residue should be calcined, redissolved in *aqua regia*, and the gold thrown down with  $\text{HNaSO}_3$  after evaporation with additional hydrochloric acid. Ferrous sulphate can also be used. The filtrate from the gold is added to the original platinum solution.

The platinum solution is then brought to 30°Bé. (ordinarily it will be stronger than that), and a 30 per cent ammonium chloride solution added, 2 l. of ammonium chloride solution per liter of platinum solution, pouring it in gradually with energetic stirring.

Allow to stand about 3 or 4 hrs., not longer, or iridium will begin to separate, and then filter off the precipitate and wash with 20 per cent ammonium chloride solution, about 1 l. of wash solution being used for each 2 l. of original platinum solution. The precipitate should be canary yellow.<sup>1</sup>

The precipitate is dried in crucibles and is then calcined about 8 hr. at between 700 and 800°C., the heat being raised gradually. Fused silica ware is best for this, as even 1 per cent of iron in a clay crucible contaminates the material with iron. The atmosphere should be strongly reducing.

The product of this calcination is known as "platinum moss." It is crushed in a mortar and boiled in 1:5 hydrochloric acid to remove any adhering iron.

If the moss is to be used to produce an agglomerated mass of platinum it should be calcined at an even higher temperature, but the temperature given is sufficient if it is to be used for platinum salts.

**Iridium Recovery.**—When the solution from the precipitation of platinum with ammonium chloride is left standing, the iridium at length comes down as  $(\text{NH}_4)_2\text{IrCl}_6$ . This is filtered, washed, dried, and calcined, giving iridium moss. The iridium moss is then treated with dilute (*i.e.*, 1:3) *aqua regia*, in which the platinum dissolves and iridium remains insoluble. The platinum solution goes back into the first stage of the process, while the decantate, filtrate and wash waters from the iridium precipitation are treated with zinc and sulphuric acid, or cast iron and sulphuric acid, throwing down all the heavy metals remaining in solution. This precipitation is known as "first blacks." See also the "lead separation" on p. 1415.

This is filtered over a vacuum, washed, dried, and put in a bone-ash cupel and roasted in a muffle. A treatment with 1:5  $\text{H}_2\text{SO}_4$  will then remove the copper, giving "cleaned blacks," which are washed by decantation.

<sup>1</sup> Thomas A. Wright says the precipitate will become contaminated with palladium on standing, and that it should not stand over five to ten minutes. Further footnotes signed T. A. W. are by Mr. Wright.

The "cleaned blacks" are then heated with dilute (1:3) *aqua regia*, giving Pt, Pd, and traces of Rh and Ir in solution, and Ir and Rh in the residue ("insoluble blacks").

Nitrates are removed and the platinum thrown down from solutions as was discussed under Treatment of Platinum Concentrates, on the preceding page. The platinum thus produced is known as "black platinum." The filtrate contains lead, rhodium, and iridium. These are thrown down again with soft iron or zinc and sulphuric acid, the precipitate being known as "second blacks," the second blacks then being roasted and cleaned with HCl (1:3) and redissolved in *aqua regia*. Evaporate to a spongy consistency with addition of HCl to get rid of the nitric-acid compounds, then dissolve the spongy mass in ammonia water. Add hydrochloric acid to acid reaction and yellow  $(\text{NH}_4)_2\text{PdCl}_6$  should come down. The filtrate carries rhodium and iridium, which should be added to the solution from the insoluble blacks.<sup>1</sup>

**Treatment of the Insoluble Blacks.**—The insoluble blacks are mixed with three times their weight of  $\text{BaO}_2$  and strongly calcined in a coke furnace for 5 or 6 hr.  $\text{Na}_2\text{O}_2$  may also be used, taking 5 to 10 times as much as there is of the residue. It is best to use fresh  $\text{Na}_2\text{O}_2$  containing little  $\text{CO}_2$ .

The mass is ground and dissolved in 15 HCl:2HNO<sub>3</sub>, using 4 l. of the mixed acid per kilogram of the mixture of blacks and barium peroxide. The solution should be feebly red.

Evaporate in porcelain to dryness so as to render insoluble the silica which has been introduced by the barium dioxide treatment. Redissolve in hot water, adding a little of 15HCl:2HNO<sub>3</sub> mix already used. Settle and decant, and wash the silica residue with hot water.

The consumption of acids can be lessened by leaching the barium dioxide fusion with hot water, discarding the solution, and treating the insoluble residue with the 15:2 HCl:HNO<sub>3</sub> mixture.

Precipitate the barium in the solution with  $\text{H}_2\text{SO}_4$  and filter off the solution. Heat the barium-free solution in porcelain on a sand bath, gradually adding  $\text{NH}_4\text{Cl}$  to saturation. Use about 300 g. of the salt per liter of liquid. After 3 or 4 hr. a purplish black precipitate of  $(\text{NH}_4)_2\text{IrCl}_6$  comes down. Filter and wash until the filtrate is only slightly colored.

The filtrate contains rhodium. It is treated with zinc or iron and sulphuric acid to produce crude rhodium ("rhodium blacks").

**Production of Osmium.**—Melt the insoluble residues from the original platinum treatment with four or five times their weight of pure zinc, and then heat for several hours at a white heat to distill off the zinc. The fumes from this distillation contain osmium and should not be inhaled.

Powder the residue from this zinc treatment and mix with three times its weight of  $\text{BaO}_2$ . Pulverize the "moss" thus obtained. Wash and dry. A train of Wolff bottles is then arranged. The first has three outlets, one used to let in a mixture of 15 parts HCl:2HNO<sub>3</sub>, as required; the second is used as a steam inlet, and the third connects to the receiving train. In practice, this flask is large enough to contain 10 kg. of moss; 15 l. HCl; 2 l. HNO<sub>3</sub>. The moss is placed in the bottle and the train connected, the acid in the above quantity admitted and steam then passed in, the bottle itself being heated. The receiving train consists of five bottles of the same

<sup>1</sup> To effect the precipitation of platinum with  $\text{NH}_4\text{Cl}$  it is always necessary to remove completely the HNO<sub>3</sub>. Otherwise palladium and iridium are precipitated also. Although palladium, when present in appreciable amounts, is precipitated with platinum whether HNO<sub>3</sub> is present or absent, in the last case it is one of occlusion. Palladium forms two salts with  $\text{NH}_4\text{Cl}$ , that of the higher state of oxidation being insoluble in excess of  $\text{NH}_4\text{Cl}$ : that of the lower state of oxidation being soluble.—T. A. W

size, in series, the first three containing water, the fourth NaOH, and the fifth  $\text{Na}_2\text{SO}_4$ . Osmium distills; iridium and ruthenium remain behind.

The iridium liquor remaining behind is precipitated hot with ammonium chloride as already described under treatment of the blacks. The ammonium chloridate is washed, filtered, dried, and calcined to moss, which is cleaned with 1:3 *aqua regia*. Platinum and palladium that have been carried along this far will dissolve and can be returned to their appropriate place in the cycle.

Take the solution of the osmium in water in porcelain, add  $\text{NH}_4\text{OH}$  to alkalinity and heat for  $1\frac{1}{2}$  hr. Filter, wash, dry, and roast the precipitate to metallic osmium. Look out for the fumes, which are dangerous.

**Iridium-ruthenium Separation.**—Reduce the ammonium-iridium chloride to "moss." Bring a mixture of 3 parts KOH and 1 part  $\text{KNO}_3$  to a quiet fusion and slowly add 1 part of the moss by weight and hold at a dark-red heat for  $1\frac{1}{2}$  to 2 hr. Cool and treat the melt with cold water.  $\text{Na}_2\text{O}_2$  can also be used and some consider it preferable.

$\text{K}_2\text{RuO}_4$  dissolves; the iridium is practically insoluble. The ruthenium is then precipitated with zinc.<sup>1</sup>

Decant and wash the iridium with sodium chlorite until solution is no longer red. Take the insoluble residue and clean it with very dilute hydrochloric acid and calcine. Wash with hot water and very dilute hydrochloric acid. Strong hydrochloric acid carries iridium into solution. Give the insoluble residue a dead roast on the filter.<sup>2</sup>

Take the filtrates and wash waters from all the above treatments and bring everything down as "blacks." Wash and calcine, then dissolve in 1:3 *aqua regia*.<sup>3</sup> This dissolves the platinum, palladium and gold<sup>4</sup> and leaves an insoluble residue of rhodium and ruthenium. The gold is precipitated with sulphur dioxide after evaporation with additional hydrochloric acid,<sup>5</sup> and the solution then treated with zinc and sulphuric acid, the precipitate, after calcining and cleaning with HCl, being almost pure palladium, providing the original separations have been carefully made.

**Melting of the Platinum Metals.**—These metals are all best melted in a crucible made of quicklime, with a cover of the same material. Platinum, like silver, absorbs a relatively large quantity of oxygen when molten. After melting the platinum, this can be burned off by reducing the oxygen blast and allowing an excess of gas to enter the furnace. Palladium is still worse.

**Lead Separation of Platinum and Iridium.**<sup>6</sup>—The metal is melted with ten times its weight of pure lead in a covered graphite crucible, in which is also placed

<sup>1</sup> See Journal American Chemical Society, December, 1925. Two articles by James Lewis Howe and associates. Separation of ruthenium and solubility of certain of its salts.

<sup>2</sup> It is very difficult to wash out the ruthenium salts with sodium hypochlorite and during the operation ruthenium is volatilized and lost. The washing is best done by decantation, as in filtering through paper, the latter becomes clogged by ruthenium reduced by the carbonaceous matter of the filter. The ruthenium is better precipitated with magnesium ribbon but keep the solution acid or it will be difficult to remove the magnesium salts. Always wash all platinum group metals precipitated as such with acidified water and in the case of both finely divided residues and precipitate it is best to use paper pulp in filtering.—T. A. W.

<sup>3</sup> Palladium is soluble with difficulty when oxidized. It should be reduced after calcining.—T. A. W.

<sup>4</sup> It also dissolves some rhodium. Note that when finely divided, freshly precipitated and unignited and undried these metals are the most readily attacked with acids. When compact or when ignited iridium, ruthenium, rhodium and osmium are difficultly soluble. This is the distinction which the literature very often fails to make therefore the cause for so-called conflicting statements. Of general interest also is the fact that rhodium is found in most all of the *aqua regia* solutions; ruthenium and osmium rarely.—T. A. W.

<sup>5</sup> Au precipitates thrown down with  $\text{SO}_2$  are contaminated with palladium and copper if the latter are present in any quantity.—T. A. W.

<sup>6</sup> From "Methods for the Recovery of Platinum, Iridium, etc., from Jewelers' Waste," Bur Mines Tech Paper 342.

enough powdered wood charcoal to cover the melt about 1 in.<sup>1</sup> The heating is conducted in a furnace and should be continued at red heat for about two hours. After the alloy has cooled it is removed and the charcoal washed off. The metal is then treated with successive portions of dilute nitric acid (1 to 5) during 4 or 5 hr. (it is well to let it digest overnight). The solution, which contains the lead and some platinum, is separated by decantation through a filter; the residue, containing iridium and platinum, is washed with dilute nitric acid and then with hot water. The filtrate and washings are evaporated until crystals begin to form; then sulphuric acid is added until no further precipitation takes place, a little more being added to be sure of an excess. The white precipitate containing part of the lead as sulphate is removed by filtration and washed with hot water. The filtrate is evaporated on a sand bath until copious white fumes come off; then it is cooled and water is added. The cold solution is filtered and the white residue containing the rest of the lead is washed with water.

The filtrates and wash waters are evaporated just to dryness and are treated with hydrochloric acid, after which the platinum may be recovered as ammonium chloroplatinate or by precipitation with metallic zinc and hydrochloric acid.

The residue from the nitric acid extraction containing the iridium and the rest of the platinum is treated for several hours with a mixture of 1 part nitric acid, 4 parts hydrochloric acid, and 9 parts water at a temperature of 80°C. It is well to let this reaction go overnight. The residue is filtered and washed with hot water and is then melted again with lead and treated as before to remove the small quantity of platinum that may still be present.

**Osmium Poisoning.**—The metal osmium must be handled with great precautions. It oxidizes slowly at room temperatures when finely divided or powdered and the oxide appears to have a sufficient volatility at ordinary temperatures to make the presence of the powdered metal in the room poisonous to some people. The oxide melts at 40°C. and boils at about 100°C. It is highly irritating to the mucous membranes and to the eyes. While the blindness (or in light poisoning cases, the intense smarting) is usually believed only temporary, and no permanent bad effects are ascribed to osmium fumes, Schoeller and Powell state that the oxide is reduced to metal by contact with the tissue "and the metallic film thus deposited on the cornea produces permanent injury to the eyesight." Osmium fumes should, therefore, be kept as much as possible under a hood and close-fitting goggles or a gas mask should be worn by any one exposed to them.

$\text{OsO}_4$  reacts with hydrochloric acid of 1.16 sp. gr., but not with weaker solutions, forming  $\text{OsCl}_4$ .

**Ruthenium.**—R. A. Cooper<sup>2</sup> says that ruthenium fumes, like those of osmium, are hard on the eyes of anyone working with them. The  $\text{RuO}_4$  begins to volatilize at about 600°C.

A concentrated solution of  $\text{RuO}_4$  will dissolve with concentrated  $\text{NH}_4\text{OH}$  to form gray-brown  $(\text{NH}_4)_2\text{RuO}_6$ .  $\text{RuO}_4$  reacts with  $\text{HCl}$  of over 1.160 density to form  $\text{RuCl}_4$ , but does not react with acid below that strength.

It should be noted that the methods as here given for the treatment of the platinum metals are essentially that given by Louis du Parc in "Le Platine du Mende," referred to in Chap. XXIX.

## APPENDIX

### METRIC—ENGLISH EQUIVALENTS

Length	Volume
1 ft. = 0.3048060096 m.	1 cu. yd. = 0.764559445 cu. m.
1 in. = 2.540005 cm.	1 cu. ft. = 0.028317 cu. m.
1 m. = 3.28083 ft. = 39.370000 in.	1 cu. in. = 16.3872 c.c.
	1 cu. ft. = 0.028316 l.
	1 cu. in. = 16.3867 ml.
	1 cu. m. = 1.3079 cu. yd.
	1 c.c. = 0.06102 cu. in.
	1 l. = 61.025 cu. in. = 0.035315 cu. ft.
Area	
1 sq. in. = 6.452 sq. cm.	
1 sq. ft. = 0.09290 sq. m.	
1 sq. yd. = 0.83613 sq. m.	
1 sq. m. = 1.1960 sq. yd. = 10.764 sq. ft.	
1 sq. cm. = 0.15500 sq. in.	

### Mass

1 lb. (Avoirdupois) = 0.4535924277 kg.	
1 oz. (Avoirdupois) = 28.3495 g.	
1 oz. (Troy) = 31.10348 g.	
1 dram (℥ = 3 ℥, apoth.) = 3.887935 g.	
1 kg. = 2.20462234 lb. (Avoirdupois) = 2.67923 lb. (Troy)	
1 g. = 0.035274 oz. (Avoirdupois) = 0.032151 oz. (Troy)	
	= 15.4324 grains

### Capacity

1 qt. (liquid) = 0.94633307 l.	
1 qt. (dry) = 1.1012 l.	
1 l. = 1.05671 qt. (liquid) = 0.9081 qt. (dry) = 33.8147 fl. oz.	
1 fl. oz. = 0.0295729 l. = 1.80469 cu. in.	
NOTE.—1 gal. (liquid) = 231.0 cu. in.	
1 bu. (dry) = 2,150.42 cu. in.	
1 l. = 1,000.027 c.c.	

### Energy

1 hp. = 0.746 kw. = 33,000 ft.-lb. per minute	
1 kw. = 1.341 hp. = 1,000 joules per second	
1 ft.-lb. = $1.383 \times 10^7$ ergs = 1.383 joules = 0.1383 kg.-m.	
1 poundal = 13,825 dynes.	
1 gram's weight = 980 dynes.	
1 pound's weight = 444,518 dynes.	
1 hp. year = 6,535 kw.-hr.	
1 kw.-yr. = 11,747 hp.-hr.	

## INTERNATIONAL ATOMIC WEIGHTS, 1924

Element	Symbol	Weight	Valence <sup>1</sup>	Electrochem. equivalents, g. per amp-hr.	Melting points, deg. C.	Boiling points deg. C., visible ebullition
Aluminum...	Al	27.0	3	0.3354	658.7	1800.0
Antimony...	Sb	120.2	3	1.4949	630.0	1460.0
Argon.....	A	89.9	0	.....	-189.3	-186.0
Arsenic.....	As	74.96	3	0.9324	850.0	450.0 <sup>2</sup>
Barium.....	Ba	137.37	2	2.5619	850.0	.....
Bismuth.....	Bi	209.0	3	2.5902	271.0	1440.0
Boron.....	B	10.9	3	.....	2350.0	3500 <sup>1</sup>
Bromine.....	Br	79.92	1	2.9814	-7.3	58.75
Cadmium.....	Cd	112.40	2	2.0955	320.9	778.0
Cæsium.....	Cs	132.81	1	.....	28.0	.....
Calcium.....	Ca	40.07	2	0.7477	810.0	.....
Carbon.....	C	12.05	4	0.1118	>3600.0	3700.0
Cerium.....	Ce	140.25	4	.....	623.0	.....
Chlorine.....	Cl	35.46	1	1.3230	-101.5	-37.6
Chromium.....	Cr	52.0	3	0.6476	1520 to >Fe	2200.0
Cobalt.....	Co	58.97	2	1.1000	1610 <sup>2</sup>	.....
Columbium.....	Cb	93.1	5	.....	1950-2200	.....
Copper.....	Cu	63.57	2	1.1858	1083.0	2100.0
Dysprosium.....	Dy	162.5	.....	.....	.....	.....
Erbium.....	Er	167.7	.....	.....	.....	.....
Europium.....	Eu	152.0	.....	.....	.....	.....
Fluorine.....	F	19.0	1	0.7085	-223.0	-187.0
Gadolinium.....	Gd	157.3	.....	.....	.....	.....
Gallium.....	Ga	70.1	.....	.....	30.1	.....
Germanium.....	Ge	72.5	.....	.....	958.0	.....
Glucinum.....	Gl	9.1	.....	.....	1280.0	.....
Gold.....	Au	197.2	3	2.4524	1063.0	2100.0
Helium.....	He	4.002	0	.....	-271.9	-268.8
Holmium.....	Ho	163.5	.....	.....	.....	.....
Hydrogen.....	H	1.008	1	0.03704	-259.0	-252.8
Indium.....	In	114.8	.....	.....	154.5	1000.0
Iodine.....	I	126.92	1	4.7353	114.0	184.35
Iridium.....	Ir	193.1	4	.....	2300.0	2850.0
Iron.....	Fe	55.84	2	1.0416	1530 ± 5	2450.0
Krypton.....	Kr	82.92	.....	.....	-169.0	-151.7
Lanthanum.....	La	139.0	.....	.....	810.0	.....
Lead.....	Pb	207.20	2	3.8654	327.4	1525.0
Lithium.....	Li	6.94	1	0.2622	186.0	500.0
Lutecium.....	Lu	175.0	.....	.....	.....	.....
Magnesium.....	Mg	24.32	2	0.4531	651.0	1120.0
Manganese.....	Mn	54.93	2	1.0255	1260 ± 20	1900.0
Mercury.....	Hg	200.6	2	7.4840	-38.87	357.0
Molybdenum.....	Mo	96.0	2	1.7900	2550.0	3350.0
Neodymium.....	Nd	144.3	.....	.....	840.0	.....
Neon.....	Ne	20.0	0	.....	-253.0	-245.9

<sup>1</sup> In those cases in which a metal has two valences, the valence given corresponds to the electrochemical equivalent, and may not necessarily be the commoner one.

<sup>2</sup> Sublimes. <sup>3</sup> Commercial metal, about 1480° C.

# APPENDIX

1419

## INTERNATIONAL ATOMIC WEIGHTS, 1924—Continued

Element	Symbol	Weight	Valence <sup>1</sup>	Electro-chem equi valents, g per amp-hr	Melting points, deg C	Boiling points deg C visible ebullition
Nickel	Ni	58.68	2	1.0946	1452 ± 3	2450 0
Niobium	Nb	222.4	0		-71 0	-62 0
Nitrogen	N	14.008	3	0.1742	-210 5	-195 7
Osmium	Os	190.9			2700 0	2950 0
Oxygen	O	16.00	2	0.2985	-218 0	-183 0
Palladium	Pd	106.7	2	1.9951	1550 0	2540 0
Phosphorus	P	31.04			44 1	287 0
Platinum	Pt	195.2	4	1.8206	1755 0	2650 0
Potassium	K	39.10	1	1.4584	62 3	667 0
Praseodymium	Pr	140.0			940 0	
Radium	Ra	226.0	2		900 0	
Rhodium	Rh	102.9			1940 0	2750 0
Rubidium	Rb	85.45			38 0	696 0
Ruthenium	Ru	101.7			>1950 0	2780 0
Samarium	Sa	150.4			1350 0	
Scandium	Sc	45.1			1200 0(?)	
Selenium	Se	79.2	2	1.477	218 5	690 0
Silicon	Si	28.1	4	0.2638	1420 0	3800 0
Silver	Ag	107.88	1	4.0258	961 0	1955 0
Sodium	Na	23.00	1	0.8582	97 5	742 0
Strontium	Sr	87.63	2	1.6333	>Ca<Ba	
Sulphur	S	32.06	2	0.5980	112 8-119 2	441 5
Tantalum	Ta	181.5			2850 0	
Tellurium	Te	127.5	2	2.370	451 0	1300 0
Terbium	Tb	159.2				
Thallium	Tl	204.0			302 0	1700 0 <sup>a</sup>
Thorium	Th	232.15			>1700 0<Pb	
Thulium	Tm	169.9				
Tin	Sn	118.7	2	2.2144	231 9	2270 0
Titanium	Ti	48.1	4	0.4490	1795 0 ± 15 0	2700 0
Tungsten	W	184.0	6	1.1437	3267 0	3700 0
Uranium	U	238.2			Near Mo	3100 0
Vanadium	V	51.0			1720 0 + 20 0	
Xenon	Xe	130.7	0		-140 0	109 1
Ytterbium	Yb	173.5			1800 0(?)	
Yttrium	Yt	89.33			1490 0	
Zinc	Zn	65.37	2	1.192	419 4	918 0
Zirconium	Zr	90.6			1700 0(?)	

NOTE.—In addition to the above elements there is some reason to believe in the existence of a gas cerium (so called from its existence in the solar corona) which would form 0.00058 per cent of the earth's atmosphere according to Dr. A. WOLFNER'S calculations (*Science* Oct. 31, 1913).

<sup>1</sup> In those cases in which a metal has two valences the valence given corresponds to the electrochemical equivalent and may not necessarily be the commoner one. Also given as 1280° C.



## POWER REQUIREMENTS—ELECTROTHERMAL INDUSTRIES

MATERIAL	KILOWATT HOURS PER TON	MATERIAL	KILOWATT HOURS PER TON
Aluminum	30,000	Ferrosilicon (75 per cent)	10,000
Alundum	2,000	Ferrotungsten (70 per cent)	7,600
Barium oxide	1,200	Ferrouuranium (40 per cent)	8,0000
Cadmium	2,500	Ferrovanadium (35 per cent)	6,8000
Calcium carbide	4 000	Graphite	7,800
Calcium cyanamide	3 750	Iron (electrothermic)	2,500
Carbon bisulphide	850	Iron (electrolytic)	4,000
Carborundum	8 500	Lead	145
Caustic soda, 2,000 lb	3,000	Magnesium	27,000
Chlorine 1,760 lb		Nitric acid	17,500
Copper (electrolytic refined)	300	Phosphorus	12,000
Copper (electrolytic)	2,600	Potassium chlorate	1,350
Ferrochromium (60 per cent)	8 000	Sodium	20,000
Ferromanganese (76 per cent)	5 000	Sodium chlorate	7,000
Ferromolybdenum (60 per cent)	8,400	Tin	175
Ferrosilicon (50 per cent)	5,000	Zinc	4,000

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